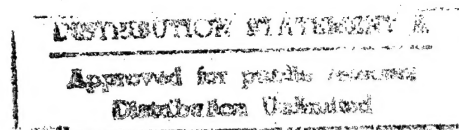# DEVELOPMENT OF POLYPHENYLQUINOXALINE GRAPHITE COMPOSITES

by

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P.M. HERGENROTHER
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THE BOEING COMPANY
AEROSPACE GROUP
SEATTLE, WASHINGTON

PREPARED FOR
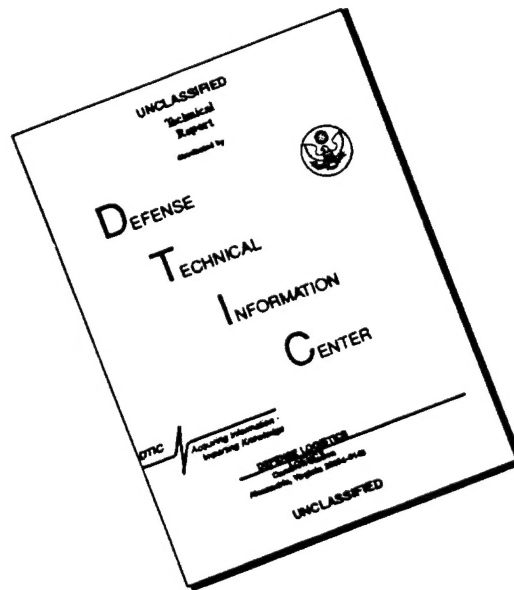
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16. Abstract

The potential of polyphenylquinoxaline (PPQ)/graphite composites to serve as structural material at 316°C (600°F) has been demonstrated using a block copolymer, BICo(1:3), PPQ derivative.

Initially, thirteen polyphenylquinoxalines were evaluated. From this work, four candidate polymers were selected for preliminary evaluation as matrices for HMS graphite fiber reinforced composites. The preliminary composite evaluation enabled selection of one of the four polymers for advanced composite preparation and testing. Using an experimentally established cure schedule for each of the four polymers, preliminary laminates of 50% resin volume content, prepared without postcure, were tested for flexure strength and modulus, interlaminar shear strength (short beam), and tensile strength and modulus at ambient temperature. A block copolymer (BI Co 1:3) derived from one mole p-bis (phenylglyoxalyl) benzene, one fourth mole 3,3'-diaminobenzidine and three-fourths mole 3,3', 4,4'-tetraminobenzophenone was selected for extensive study. Tensile, flexural, and interlaminar shear values were obtained after aging and testing postcured BI Co (1:3) laminates at 316°C (600°F).

The potential of PPQ/graphite laminates to serve as short term structural materials at temperatures up to 371°C (700°F) was demonstrated through weight loss experiments.

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FOREWORD

This report presents the work accomplished by The Boeing Company during
the period of July 1, 1971, to September 30, 1972, on NASA Contract
NAS 3-15547, "Development of Polyphenylquinoxaline Graphite Composites."
The work was administered by the National Aeronautics and Space Administration,
Lewis Research Center, Aeronautics Procurement Section, Cleveland, Ohio,
with Dr. P. Delvigs as Project Manager.

Performance of this contract was under the direction of the Aerospace Group,
The Boeing Company; Dr. R. G. Cheatham, Program Supervisor, and
Mr. J. T. Hoggatt, Program Technical Leader. Principal investigators on the
program were Mr. P. M. Hergenrother, Polymer Synthesis and Characterization,
and Dr. José G. Shdo, Composite Fabrication and Evaluation.

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1.0 INTRODUCTION

The urgent need for new improved structural resins which meet the requirements of advanced aircraft and space vehicles has served as the impetus for research in the area of high temperature, high performance composites. During the last ten years, a variety of new thermally stable heterocyclic aromatic polymers have been prepared. From this effort, the polyquinoxalines have evolved which represent one of the more promising heterocyclic polymer systems currently known for potential use in structural applications that demand high thermal, oxidative, and/or hydrolytic stability.

The synthetic route to polyquinoxalines (PQ) was initially proposed by Sorenson (Ref. 1) in 1961, at a meeting of the American Chemical Society. At that time, Stille commented on the status of his work already underway on PQ which led to a series of papers (Ref. 2-4). Concurrent with Stille's work, deGaudemaris and coworkers (Ref. 5 and 6) were also investigating PQ through the same synthetic route. In 1963, work began under Navy sponsorship to demonstrate the potential of PQ for use as high temperature structural resin (Ref. 7). This work principally concerned the development of a synthetic procedure to obtain a reproducible processable polymer and the evaluation of PQ as a laminating resin and adhesive (Ref. 8).

In an attempt to improve the overall thermaloxidative stability of PQ, polyphenyl-quinoxalines (PPQ) were prepared (Ref. 9 and 10). The PPQ offered several distinct advantages over the PQ, such as easier synthesis, improved processability, and improved thermaloxidative stability which is summarized in a review on linear poly-quinoxalines (Ref. 11). The present program was conducted to establish the utility of PPQ as matrix resins for high modulus graphite reinforced composites. The fiber chosen for this particular study was HM-S type graphite fiber ($E = 60 \times 10^6$ psi). It was

1.0 (Continued)

assumed that any processing knowledge and data obtained with this material could be
translated readily to the other graphite types. Two basic PPQ were selected on the
basis of available data for study in this program. These PPQ represented the most
promising polymers, at the time, for potential use as resin matrices in graphite
composites for long term performance (e.g., 1000 hours) at 316°C (600°F) in air.
Twelve molecular weight versions, including copolymers from two basic PPQs,
were evaluated. In addition, one other PPQ, a monoether PPQ (MEPPQ), was
selected primarily on the basis of its processability which had been demonstrated
in adhesive studies (Ref. 12) and preliminary composite work, for a total of
thirteen polymers.

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2.0   SUMMARY

Thirteen polyphenylquinoxalines (PPQ) were synthesized and characterized in terms of solution viscosity, melt temperature, ultraviolet spectra, dielectric loss, elevated temperature aging, and flow and wetting characteristics. In addition, four polymers selected from the screening study were subjected to preliminary evaluation as matrices for HMS graphite fiber reinforced composites.

A preliminary composite evaluation was conducted to enable selection of one of the four polymers for advanced composite preparation and testing. Using an experimentally established cure schedule for each of the four polymers, 'unidirectional laminates of 50% resin volume content were prepared (without postcure) and their room temperature, 204°C (400°F), and 316°C (600°F) mechanical properties determined in terms of flexure strength and modulus, short beam interlaminar shear (ILS) strength, and tensile strength and modulus. In addition, tests were conducted to determine laminate weight loss due to accelerated aging at an elevated temperature of 371°C (700°F). Nominal flexure strength of 6.5×10^8 N/m^2 (9.5×10^4 psi) and flexure modulus of 7×10^{10} N/m^2 (10×10^6 psi), interlaminar shear strength (ILS) of 3.2×10^7 (4.5×10^3 psi) and tensile strength of 7×10^8 N/m^2 (1.02×10^5 psi) were obtained at ambient temperature on the unpostcured composites . Although there were nominal, small decreases on these mechanical properties at 204°C (400°F), at 316°C (600°F) all values were low. This was attributed to not postcuring the laminates. After aging 72 hours at 371°C (700°F), laminates, derived from each of the four polymers, displayed weight losses ranging between 3.8% to 5%, however nominal laminate weight losses of 52% resulted on extending the 371°C (700°F) aging to 500 hours. The results of the physical property tests and weight retention due to the 72 hours exposure at 371°C (700°F) were used to select one polymer system for postcure studies. The selected polymer was a block copolymer derived from one mole p-bis(phenylglyoxalyl)benzene, one fourth mole 3,3'—diaminobenzidine and three-fourths mole 3,3', 4,4'—tetraminobenzophenone, designated as BICo (1:3).

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2.0   (Continued)

Postcure studies, conducted on laminates derived from the selected polymer, yielded advanced composites having improved retention of physical properties at 204°C (400°F) and 316°C (600°F):

Virtually no decrease in ILS resulted due to aging BlCo (1:3) laminates for 1000 hours at 204°C (400°F). The average ILS strength was 2.9×10^7 N/m^2 (4220 psi) at room temperature compared to 2.8×10^7 N/m^2 (4060 psi) after 1000 hours of exposure and testing at 204°C (400°F). The tensile strength at room temperature was 7.0×10^8 N/m^2 (101,500 psi), compared to 7.1×10^8 N/m^2 (103,600 psi) after 1000 hours of exposure and testing at 204°C (400°F). The flexural strength at 204°C (400°F) was 6.1×10^8 N/m^2 (88,900 psi) after 1000 hours of exposure at 204°C (400°F), compared to 8.3×10^8 N/m^2 (120,800 psi) at room temperature.

After exposure of 500 hours at 316°C (600°F) and testing at 316°C (600°F), laminate ILS strength values of 1.9×10^7 N/m^2 (2780 psi) were obtained. Laminate tensile and flexure strength values of 4.9×10^8 N/m^2 (70,600 psi) and 3.6×10^8 N/m^2 (51,900 psi), respectively, were obtained at 316°C (600°F) after exposure of 500 hours, at 316°C (600°F). Due to loss of some of their matrix polymer, the mechanical properties of test specimens that aged 1000 hours at 316°C (600°F) were not determined. In separate experiments BlCo (1:3) laminate weight loss was determined to be 16% after aging 1000 hours at 316°C (600°F). A weight loss of less than 1% was obtained on aging BlCo (1:3) laminates 1000 hours at 204°C (400°F). On aging 1100 hours at 316°C (600°F) BlCo (1:3) films exhibited a weight loss of 1.24%. After 100 hours at 371°C (700°F) the block copolymer exhibited a weight loss of 11.4%.

Thermal cycling tests were conducted on BlCo(1:3) laminates. Test specimens were cycled one hundred times between –54°C (–65°F) and 316°C (600°F). Laminate damage, such as crazing or cracking, resulting from the exposure, was not observed. The room

2.0   (Continued)

temperature tensile strength of thermally cycled specimens was 6.4×10^8 N/m^2 (92,700 psi) compared to 7.0×10^8 N/m^2 (101,500 psi) for non-exposed laminates.

BICo (1:3) laminate resistance to creep was determined through 200 hour creep tests at room temperature and 260°C (500°F). A static load of 50% ultimate stress for BICo (1:3) laminates did not produce measurable creep at room temperature or 260°C (500°F).

The hydrolytic stability of BICo (1:3) laminates was determined. Short beam inter-laminar shear (ILS) specimens gave, after standing in boiling water for two hours, room temperature ILS strength values of 4.0×10^7 N/m^2 (5760 psi). This compares to 2.9×10^7 N/m^2 (4220 psi) ILS strength values obtained from control specimens tested at room temperature

The thermal expansion between -196°C (-320°F) and 316°C (600°F) was determined for each of the three principal axes of BICo (1:3) laminates. Results of the thermal expansion tests, and details of the foregoing summary, including mechanical property tests of 0°/90° laminates, are discussed within the body of this report.

Thirteen different polyphenylquinoxalines (PPQ) were initially synthesized and characterized in Task I of this program.   These consisted of homopolymers from the reaction of p–bis (phenylglyoxalyl)benzene   (I) with 3,3'–diaminobenzidine (II) or with 3,3', 4,4' – tetraaminobenzophenone (III) to yield PPQ–I and PPQ–II respectively (Eq. 1) and also of block and random type copolymers containing various degrees of PPQ–I and PPQ–II character.

PPQ–I AND ISOMERS

PPQ–II

$$(1)$$
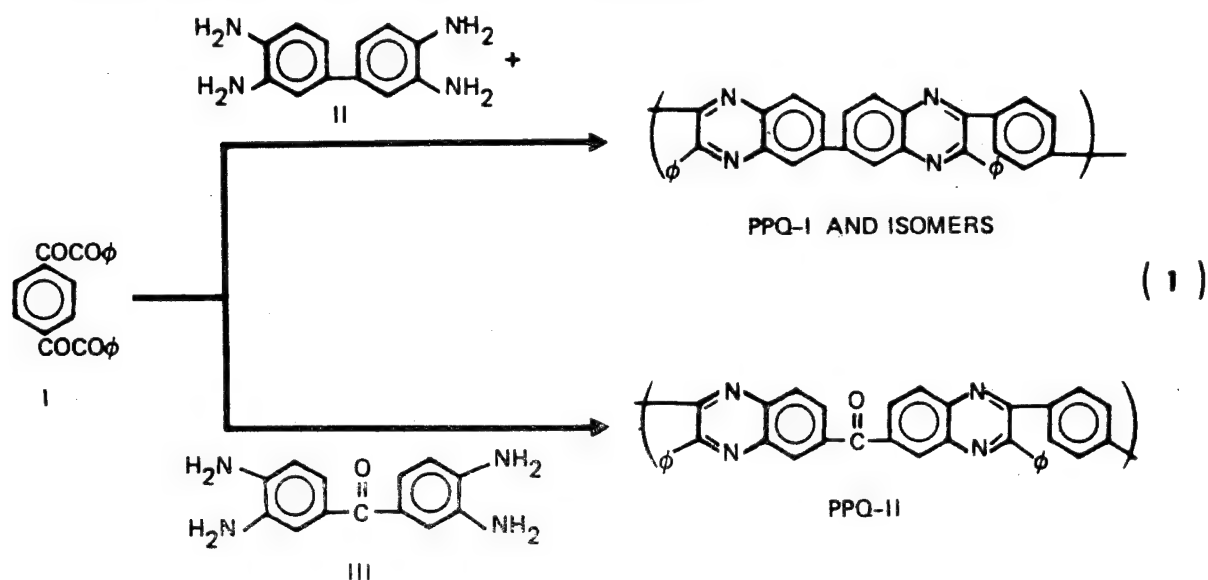
The monoether PPQ (MEPPQ) was prepared from the reaction of 3,3' diaminoben- zidine (II) with p,p' –oxydibenzil (IV) as shown in Eq. 2.

MEPPQ

$$(2)$$

3.0   (Continued)
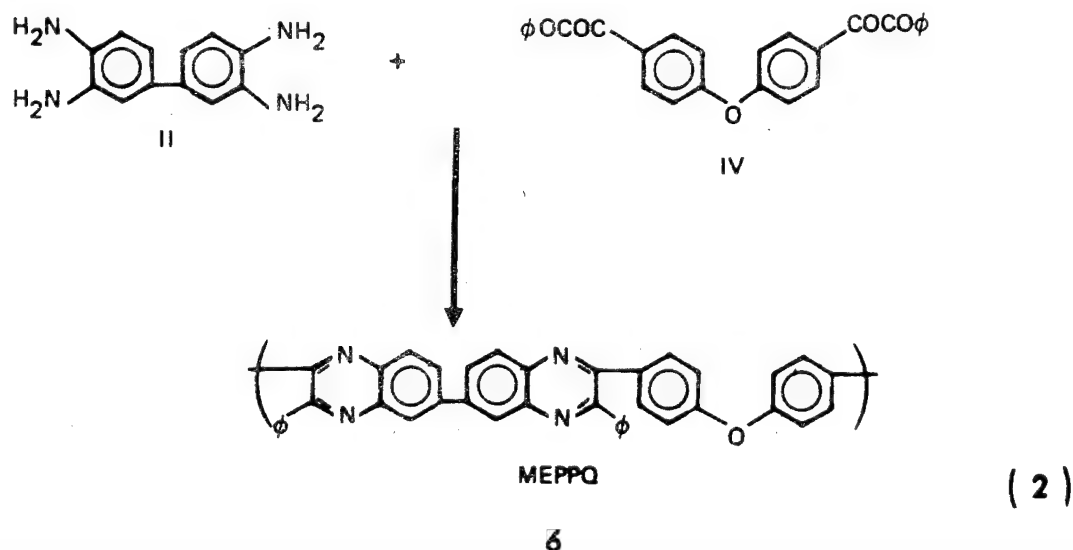
More specifically, the thirteen polymers consisted of the following:

o   a low, intermediate, and high molecular weight version of
     PPQ-1 (3 polymers)

o   a low, intermediate and high molecular weight version of
     PPQ-II (3 polymers)

o   Random type copolymers (RaCo) consisting of various degrees of
     PPQ-I and PPQ-II character* (3 polymers)

o   Block type copolymers (BlCo) consisting of various degrees of PPQ-I
     and PPQ-II character* (3 polymers)

o   Monoether PPQ (MEPPQ) (1 polymer)

The low, intermediate, and high molecular weight versions of the homopolymers
corresponded to inherent viscosities (η_{inh}, 0.5% H_2SO_4 at 25°C) of 1.0,
1.0 to 2.0, and   2.0 dl/g respectively. The synthesis of the copolymers used
the stoichiometry as indicated in Table I.

TABLE I

MOLAR AMOUNTS OF REACTANTS IN COPOLYMER SYNTHESIS

Reactant			
I	II	III	Polymer
1.00	0.75	0.25	Random Co (3:1), Block Co(3:1)**
1.00	0.50	0.50	Random Co(1:1), Block Co (1:1)
1.00	0.25	0.75	Random Co (1:3), Block Co(1:3)

From these thirteen polymers, four PPQ were selected for preliminary composite
evaluation in Task II. One of the four PPQ in Task II was then selected for
more comprehensive composite evaluation in Task III. The following paragraphs
describe the synthesis, characterization and composite studies performed under
this task.

*   Structures are based on synthetic approach.

**Designates ratio of PPQ-1 and PPQ-II in polymer as shown in equation 1.

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3.1   Polymer Synthesis

As shown in equation 1, PPQ I and PPQ II are prepared from the reaction of p-bis (phenylglyoxalyl) benzene (I) with 3,3'-diaminobenzidine (II) or with 3,3', 4,4' -tetraaminobenzophenone (III) to yield the respective polymers. The p-bis (phenylglyoxalyl)benzene was prepared through an established route (Ref. 13) as shown in Eq. 3. The two aromatic tetraamines were obtained commercially and recrystallized prior to use (Section 6.1 Appendix) in polymer synthesis. The p-bis (phenylglyoxalyl)benzene and the two tetraamines were used in 12 of the 13 polymers. The one remaining polymer, the MEPPQ, was synthesized from the reaction of 3,3'-diaminobenzidine with p,p'-oxydibenzil (IV) as shown in Eq. 2. The p,p'-oxydibenzil was synthesized as shown in Eq. 4 (Ref. 14).

$$(\mathbf{3})$$

$$(\mathbf{4})$$

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3.1 (Continued)
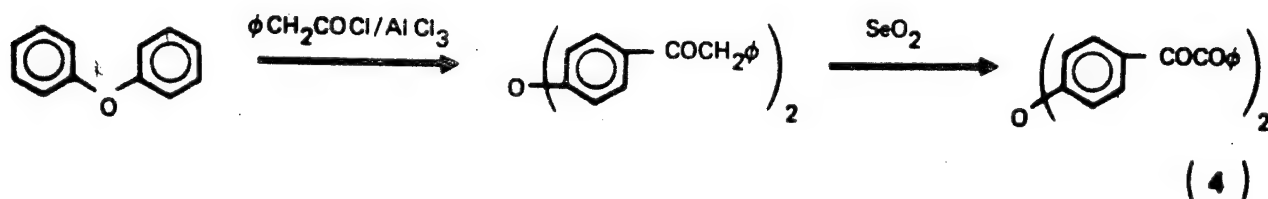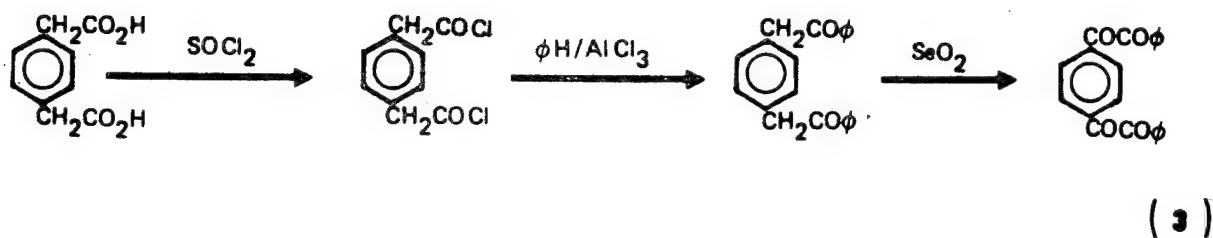
Detailed polymer synthesis procedures are given in Section 8.1 (Appendix). In general; however, the polymer preparation involved the addition of the tetracarbonyl reactant as a fine powder to a slurry of the tetraamine in a 1:1 mixture of m - cresol and xylene at a temperature of <35°C over a period of approximately 5 minutes. Preliminary polymer synthesis using high purity reactants showed that stoichiometric quantities of reactants on a 0.010 mole scale at 15 to 20% solids content (based upon weight of reactants and volume of solvent) generally gave very viscous to extremely viscous solution and in some cases, gelation. The gelling problem in condensation polymers may be attributed to factors such as molecular weight, branching, or polymer association. The gelling phenomenon can be alleviated without appreciable detrimental effect upon the polymer structure or properties by upsetting the stoichiometry of the reactants. The stoichiometry should be upset preferably in favor of the tetracarbonyl reactant since PPQ with amino end groups tend to display poorer thermaloxidative stability. As shown in Table 2, when the stoichiometry was upset by 2% in favor of the tetracarbonyl reactant (polymer Nos. 2, 3, 6, 7, and 13), polymers with inherent viscosities as high as 1.84 dl/g (polymer No. 13) were obtained. This was unexpected because stoichiometric quantities of reactants are generally required to form high molecular weight polymers (excluding interfacial condensation). The following is a plausible explanation of the unexpected results. Similar to poly-as-triazine, (Ref. 15) PPQ polycondensation exhibits many features of an interfacial polycondensation and as explained by Morgan (Ref. 16), the rate of polymerization is faster than the rate of mixing or dissolution such that there may be temporary interfaces within which the polycondensation is proceeding independently of the stoichiometry of the two reactants in the complete system. The tetracarbonyl reactant is more soluble in the solvent mixture than the tetraamine.

In some cases, when the stoichiometry was upset by 2% in favor of the tetracarbonyl reactant, the solution viscosity became extremely high prior to the formation of a complete solution (particles present identified as tetraamine).

Table 2: PHYSICAL CHARACTERIZATION OF POLYPHENYLQUINOXALINES FOR TASK I

POLYMER NO.	SAMPLE NO. PH-1	POLYMER	STOICHIOMETRY NH$_2$/CO [1]	RX SCALE (MOLE)	CONC % SOLIDS [2]	SOL'N VISCOSITY, CPS AFTER [3] 3 DAYS	SOL'N VISCOSITY, CPS AFTER [3] ~74 DAYS	η_{inh}, dl/g [4]	UV SPECTRAL DATA [5] λ_{MAX}, mμ	UV SPECTRAL DATA [5] ϵ
1	P132-1	HMW PPQ-I	1.00/1.00	0.01	20.0	GELLED	—	2.40	2.40	44,350
2	105-1	IMW PPQ-I	0.98/1.00	0.05	18.7	58,000	65,600	1.24	292	43,911
3	106	LMW PPQ-I	0.98/1.00	0.10	17.6	6,880	7,250	0.83	292	43,110
4	P134-II	HMW PPQ-II	1.00/0.98	0.10	17.0	83,000	112,000	2.39	282	58,050
5	105-2	IMW PPQ-II	0.99/1.00	0.05	20.0	30,000	33,000	1.14	282	57,794
6	P135-II	LMW PPQ-II	0.98/1.00	0.05	20.0	1,000	1,400	0.70	282	56,896
7	107-2	RaCo (3:1)	0.98/1.00	0.05	20.0	7,800	9,200	0.87	287	46,160
8	108	RaCo (1:1)	1.00/1.00	0.05	20.0	84,200	95,400	1.55	285	49,376
9	107-3	RaCo (1:3)	0.99/1.00	0.05	20.0	8,400	8,800	1.04	283	54,122
10	110-2	BiCo (3:1)	1.00/1.00	0.05	13.4	107,000	119,400	1.89	287.5	44,739
11	110-1	BiCo (1:1)	1.00/1.00	0.05	17.4	81,000	88,800	2.41	285	47,880
12	110-3	BiCo (1:3)	1.00/1.00	0.05	15.5	24,000	27,200	1.92	283	52,099
13	P137-1S	MEPPQ	0.98/1.00	0.20	18.0	300,000	—	1.84	293	45,553
14	113-1	PPQ-I	0.985/1.000	0.02	16.4	9,000	—	0.97	—	—
15 [6]	113-2	PPQ-I	0.985/1.000	0.02	17.7	14,000	—	0.91	—	—
16 [7]	P135-I-1	PPQ-I	0.97/1.00	0.05	20.0	69,200	—	0.86	—	—
17 [7]	109	BiCo 2:3	1.00/1.00	0.05	17.6	94,400	—	1.93	—	—

1. MOLAR AMOUNT OF TETRAAMINE TO TETRACARBONYL; SOLVENT, 1:1 M-CRESOL AND XYLENE
2. CONCENTRATION BASED UPON REACTANTS BY WEIGHT
3. BROOKFIELD VISCOSITY AT 25°C
4. INHERENT VISCOSITY (0.5% H$_2$SO$_4$ AT 25°C), POLYMER PPT IN MeOH, DRIED ~130°C IN VACUO 4 HRS
5. ULTRAVIOLET SPECTRUM DETERMINED IN H$_2$SO$_4$; λ_{MAX} = WAVELENGTH OF MAXIMUM ABSORPTION; ϵ = EXTINCTION COEFFICIENT (MOLAR ABSORPTIVITY)
6. SOLVENT, SYM-TETRACHLOROETHANE
7. POLYMERS SUBSTITUTED IN PRELIMINARY COMPOSITE EVALUATION IN PLACE OF HMW-PPQI AND II

3.1   (Continued)

Random copolymers (polymers Nos. 7, 8, and 9) were prepared by adding p-bis (phenylglyoxalyl) benzene to a slurry of the two tetraamines according to the stoichiometry given in Table I. Since 3,3'-diaminobenzidine is more reactive with the tetracarbonyl compound than 3,3' 4,4'-tetraaminobenzophenone, the random copolymers may contain a high degree of block character. The random copolymers (Polymers No. 7, 8 and 9) were prepared by upsetting the stoichiometry from 0 to 2% in favor of the tetracarbonyl reactant to yield copolymers having Brookfield solution viscoisities of 7,800, 8,400 and 84,200 centipoises and η_{inh} of 0.87, 1.04, and 1.55 dl/g respectively. The solutions of the random copolymers appeared to be stable and exhibited no detectable gel structure even at exact stoichiometry (Polymer No. 8).

Block copolymer synthesis involved the preparation of low molecular weight forms (oligomers) of PPQ-I and PPQ-II. The stoichiometry was adjusted to yield one oligomer rich in amino end groups while the other oligomer was rich in carbonyl end groups. The overall stoichiometry was balanced. The oligomeric solutions were blended and the blend further reacted to provide block copolymers. The degree of PPQ-I, and PPQ-II character was controlled by the relative amounts of each tetraamine used. As indicated in Table I, a distribution ratio for PPQ-I and PPQ-II was 3:1, 1:1, and 1:3, respectively. The block copolymers were prepared using exact stoichiometry at 20% solids content. However, the solutions became extremely viscous after stirring and were diluted to solids content of 13.4 to 17.4% (polymers No. 10, 11, and 12).

The MEPPQ was initally prepared on a 0.05 mole scale at 18% solids content by upsetting the stoichiometry by 2% in favor of the tetracarbonyl reactant. The resulting solution was viscous and the polymer exhibited an η_{inh} of 1.23 dl/g. However, when the synthesis was repeated on a 0.20 mole scale (polymer No. 13) the solution viscosity became extremely high (Brookfield viscosity of 300,000 centipoises). No reasonable explanation is offered to account for this result. The

3.1   (Continued)

preparation of this polymer was repeated later to provide a stable solution having a
viscosity of 18,600 cps. The other properties of this polymer were essentially the
same as those of polymer No. 13.

3.2   Polymer Characterization

Each of the thirteen polymers were subjected to characterization tests; the results of
which are described below.

a.   Viscosity

As shown in Table 2, the solution viscosity of eleven (polymers No. 2 through
12) of the thirteen proposed polymers increased upon standing at ambient tempera-
ture during the first 70 days. However, the solutions stabilized and no further
increase in the solution viscosity was observed after standing an additional 3
months.

The inherent viscosity of each polymer is given in Table 2.

b.   Ultraviolet Spectroscopy

Ultraviolet spectroscopic study of the polymers showed that the λ_{max} for
PPQ-I and PPQ-II are at 292 and 282 mμ respectively and the λ_{max} of the
various copolymers occur between these two wavelengths.

The molar absorptivity (ϵ) of PPQ-II is greater than that of PPQ-I. For example,
ϵ for high molecular weight versions of PPQ-I and PPQ-II are 44,350 and
58,050 respectively. The trend in the copolymer series is as expected. As the
amount of PPQ-II character increases, the λ_{max} decreases and ϵ becomes
greater. The ultraviolet spectra of representative PPQ are shown in Figures 1,
2, and 3.

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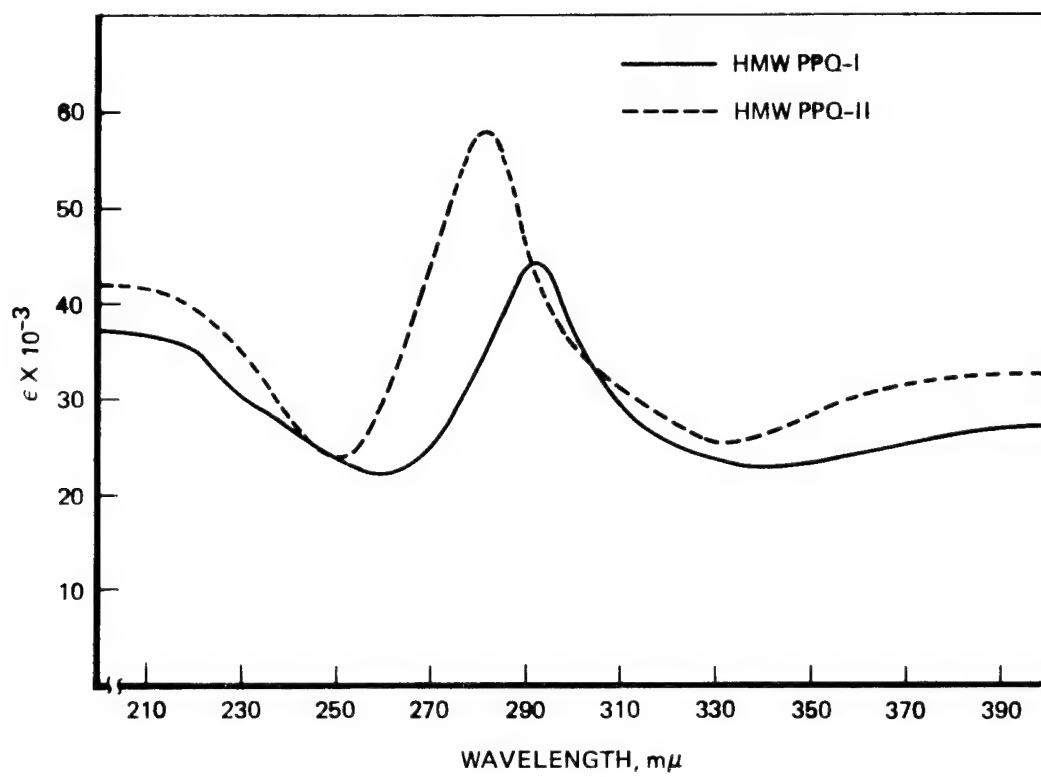
Figure 1: ULTRAVIOLET SPECTRA OF POLYPHENYLQUINOXALINES (IN H_2SO_4)
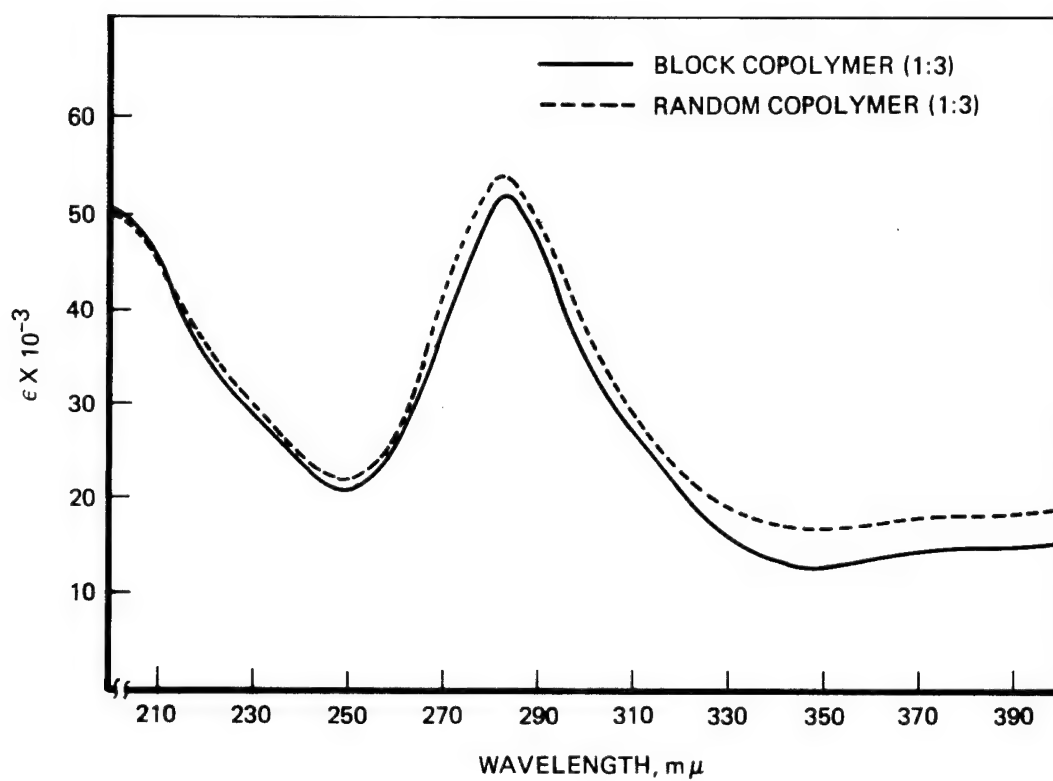
Figure 2: ULTRAVIOLET SPECTRA OF POLYPHENYLQUINOXALINES (IN H_2SO_4)

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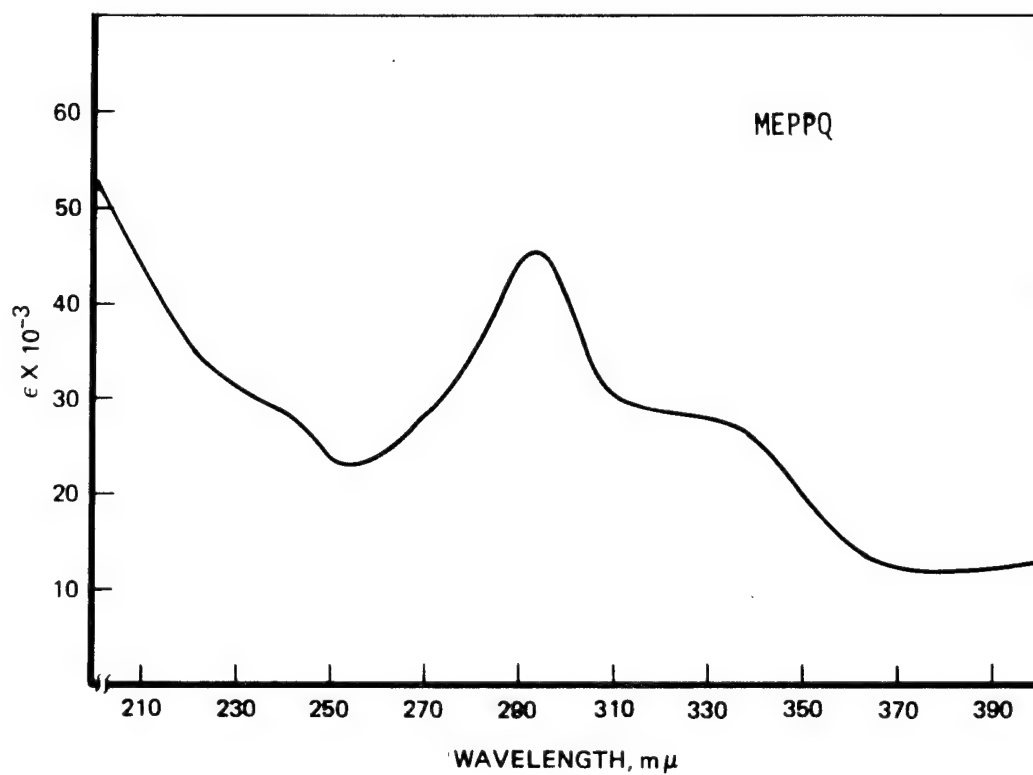
Figure 3: ULTRAVIOLET SPECTRUM OF POLYPHENYLQUINOXALINE (IN H_2SO_4)

3.2   (Continued)

c.   Polymer Melt Temperature

The thermal properties of the thirteen polymers are shown in Table 3. The poly-
mer softening temperatures (PST) were determined by applying spatula pressure
to a polymer sample sandwiched between cover slips which had been placed onto
a preheated Fisher Johns Melting Point Apparatus. The temperature range where
the opaque sample softened and became almost completely transparent was taken
as the PST. This is a good test for rough screening only, because the method is
subject to variations due to sample size, ΔT, and pressure and individual tech-
nique. As a result, the PST of the low, intermediate, and high molecular ver-
sions of PPQ-I and PPQ-II failed to show any pronounced differences even though
small differences obviously exist.

d.   Glass Transition Temperature

The glass transition temperature (Tg) was determined by Differential Scanning
Calorimetry (DSC) at a heating rate of $20^{\circ}C$/min. in nitrogen. A typical DSC
curve is shown in Figure 4 for a block copolymer (Polymer No. 12). The sample
was initially cycled to $400^{\circ}C$ in an inert atmosphere and showed a broad endo-
therm at $\sim 80^{\circ}C$ which was attributed to the release of water and/or solvent.
Upon a rerun, no endotherm was observed and the Tg was taken as the inflection
point of the ΔT versus temperature curve.

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Table 3: THERMAL CHARACTERIZATION OF POLYPHENYLQUINOXALINES FOR TASK I

POLYMER NO.	PST (°C) [1]	Tg (°C) [2]	FILM THICKNESS (mm)	WT LOSS(%) AFTER TIME (HRS) AT 316°C IN AIR [3] 25	1100	ACT WT LOSS	LIGHT TRANS(%) AFTER TIME(HRS) AT 316°C IN AIR [3] 0	614	1100	FLEXIBILITY, FAILURE AFTER TIME (HRS) AT 316°C [4]	WT LOSS(%) AFTER TIME (HRS) AT 371°C IN AIR [3] 25	~100	151	226	POLYMER FUSION AT TEMP(°C) 1-GOOD 3-POOR 5-VERYLITTLE [5] 343 (650°F)	371 (700°F)	399 (750°F)
1	>340	370	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
2	335-41	350	.0330	7.49	12.12	4.63	67	36	20	>259<330	7.0	38.4	–	–	5	2	1
3	330-39	335	.0483	4.51	11.72	7.21	60	20	5	>187<259	5.7	34.3	–	–	2	1	1
4	300-10	325	.0483	8.37	13.43	5.06	65	35	–	>631<1100	10.1	15.1	–	46.6	2	1	2
5	300-08	314	.0660	7.20	9.67	2.47	67	37	20	>187<259	8.6	16.4	51.4	–	1	1	1
6	295-305	310	.0559	7.31	11.94	4.63	65	31	–	>187<259	8.9	18.1	–	51.3	1	4	5
7	325-35	337	.0610	7.04	16.89	9.67	70	22	–	>168<360	8.5	18.8	–	93.2	4	3	3
8	320-31	335	.0559	6.09	12.27	6.18	62	23	11	>614<1100	6.8	13.4	23.1	–	5	2	3
9	317-28	325	.0660	6.08	12.41	6.33	56	22	–	>168<360	8.5	16.3	–	82.0	2	1	2
10	326-38	352	.0584	9.97	17.83	7.86	59	6	–	>168<360	9.4	18.0	–	95.5	5	3	5
11	323-35	335	.0483	8.28	10.81	2.53	62	35	–	>631<1100	9.0	13.4	–	80.2	3	5	4
12	316-24	327	.0533	7.50	8.74	1.24	62	44	–	>631<1100	7.5	11.4	–	71.1	2	2	2
13	317-25	290	.0711	6.61	78.04	71.43	46	–	–	>25<72	10.3	7.5	–	–	4	2	5
14 [6]	–	365	.0381 / .0381	5.70 / 8.24	12.52 / 46.91	6.82 / 38.67	61 / 61	30 / 9	–	>348<686 / >168<348	7.1 / 8.1	65.6 / 81.1	–	–	–	–	–
15	–	342	.0432	13.40	33.49	20.09	65	8	–	>168<348	13.2	58.1	–	–	–	–	–
16	330-340	337	–	–	–	–	–	–	–	–	–	–	–	–	2	1	1
17	305-315	327	–	–	–	–	–	–	–	–	–	–	–	–	2	1	2

△ 1. POLYMER SOFTENING TEMPERATURE, DETERMINED ON FISHER-JOHNS MELTING POINT APPARATUS WITH SLIGHT PRESSURE
2. GLASS TRANSITION TEMPERATURE, DETERMINED BY DIFFERENTIAL SCANNING CALORIMETRY AT $\Delta T = 20°$ C/MIN IN N_2
3. WEIGHT LOSS DETERMINED ON FILMS IN CIRCULATING AIR
4. FLEXIBILITY MEASURED BY HARD FINGERNAIL CREASE
5. FUSION TEST PERFORMED ON POWDERED SAMPLES SANDWICHED BETWEEN Aℓ, PLACED IN PREHEATED PRESS UNDER PRESSURE ~1.38x10^6 N/m^2 (200 PSI)
6. TWO FILMS, ONE INITIALLY, OTHER AFTER 3 DAYS, DRYING CONDITIONS SAME, LATTER FILM EXHIBITED HIGHER WEIGHT LOSS

17
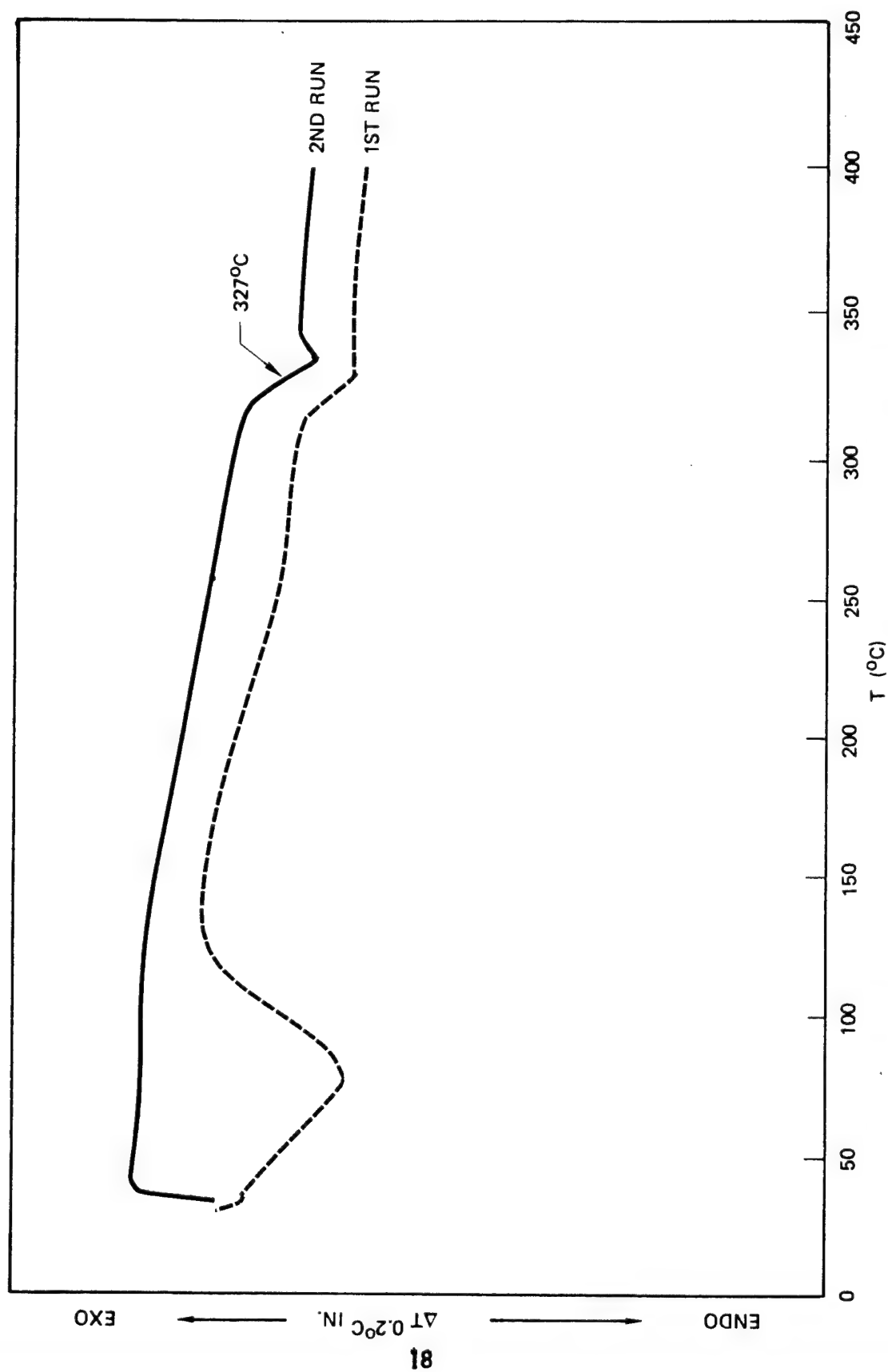
Figure 4 : DIFFERENTIAL SCANNING CALORIMETER SPECTRUM FOR BLOCK COPOLYMER (1:3)

3.2   (Continued)

The Tg of the various polymers corresponded well with the expected values.
The Tg of high molecular weight PPQ-I (Polymer No. 1) was highest (370°C)
and the Tg of low molecular weight PPQ-II (Polymer No. 16) was lowest,
(310°C) with the Tgs of the other forms of PPQ-I and II being in between.
In addition, the Tg of the copolymers came out as anticipated. For example,
in the block series, the polymer (Polymer No. 10) containing the highest
percent of the more rigid moiety (biphenylene) exhibited the highest Tg
(352°C) in this series while the polymer (Polymer No. 12) containing the
highest degree of flexible moiety (benzophenone) exhibited the lowest Tg
(327°C). The polymer containing equal portions of biphenylene and benzo-
phenone moieties exhibited a Tg of 335°C, in between the other two.

Since even low molecular weight versions of PPQ-I and PPQ-II were of
sufficiently high molecular weight to provide tough, fingernail creaseable
films, it was surprising to observe the wide spread in Tg (337°C to 370°C)
from low molecular weight to high molecular weight versions of PPQ-I.
A curve of the apparent dependency of Tg on molecular weight (as measured
by η_{inh}) of PPQ-I is shown in Figure 5. At η_{inh} of ~2.2 dl/g the Tg
for this particular polymer appears to level off.

The Tg of IMW PPQ-I and IMW PPQ-II was also determined by Dynamic
Scanning Dielectrometry (DSD) on films using an Audrey II which measures
changes in capacitance and dissipation factor over a frequency range from
100 to 1000 cycles per second as a function of time. A typical curve is
shown in Figure 6. The Tg was taken as the temperature where the
capacitance curve changed its slope (336°C). This generally coincides with
the intercept of the temperature versus dissipation factor curve at 100 cycles/
second. Prior to a Tg determination, the polymer films were cycled in the
dielectric test apparatus to 350°C in nitrogen to remove residual solvent and/
or water.   For PPQ-I and PPQ-II (Polymers No. 2 and 5), DSC provided
Tgs of 350 and 314°C whereas DSD provided Tg of 336 and 310°C respectively.
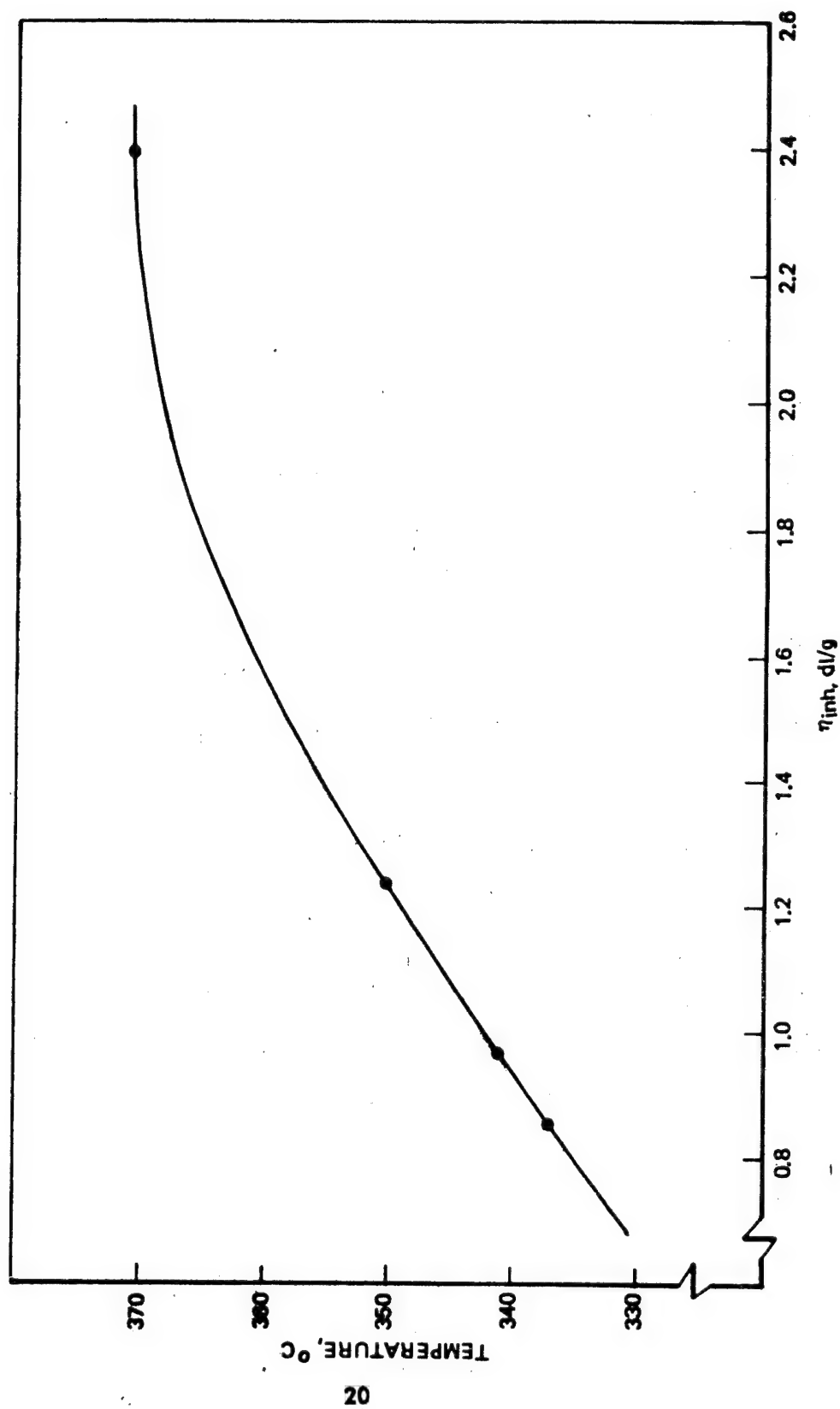
Figure 5 : PLOT OF T_g VERSUS INHERENT VISCOSITY OF PPQ-I

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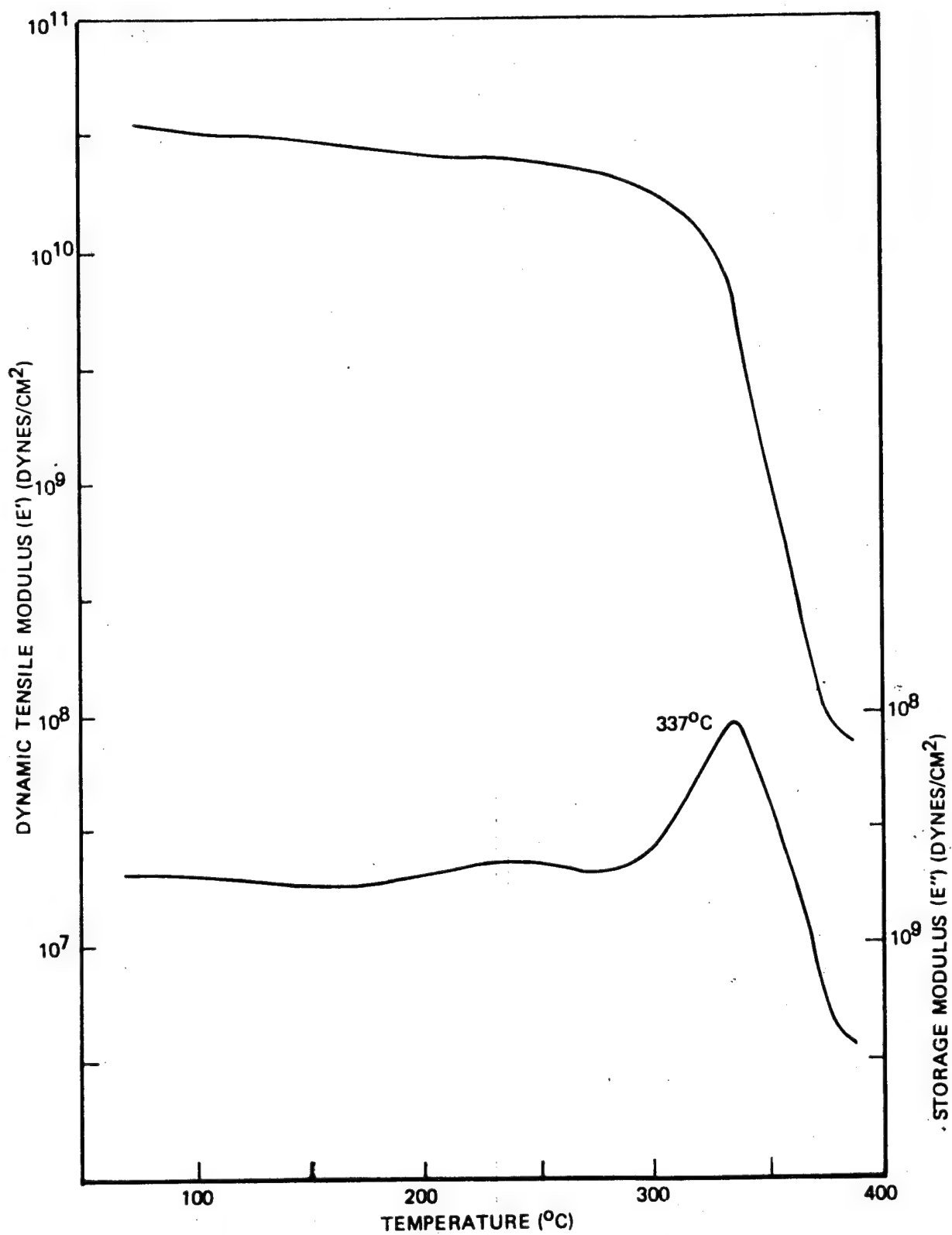
Figure 6: DYNAMIC MECHANICAL RELAXATION SPECTRUM OF PPQ 1

3.2   (Continued)

e.   Isothermal Aging Studies

The thermaloxidative stability of the PPQ listed in Table 3 and 4 were determined
by measuring the retention of weight, color, and flexibility of their film after
isothermal aging in circulating air at 316°C (600°F) and 371°C (700°F) respec-
tively. The polymer films were prepared by doctoring the polymer solution
onto a glass plate followed by drying overnight at 70°C in air and then at
~130°C in vacuo for 4 hours. All of the polymers readily formed tough
flexible transparent yellow films. However, the toughness of the low molecu-
lar weight PPQ-II film (Polymer No. 6) was less than that of the other films.
No aging was performed on high molecular weight PPQ-I because the solution
gelled rendering film formation impossible. All of the films exhibited an
initial weight loss after 25 hours aging at 316°C (600°F) and 371°C (700°F)
which is tentatively attributed to the loss of residual solvent and water. At
316°C (600°F) in circulating air, the actual weight loss on the polymers
varied from the lowest of 1.24% for the block copolymer 1:3 (polymer
No. 12) to the highest of 71.43% for the MEPPQ (polymer No. 13) after
1100 hours. The excellent thermaloxidative stability of the polymers (excluding
the MEPPQ) is also reflected in the retention of film flexibility and light
transmission. Several of the polymers (No. 4, 8, 11, and 12) retained
fingernail creaseability after more than 614 hours at 316°C (600°F) in air.

At 371°C (700°F) in circulating air, the block copolymer (1:3, polymer No.
12) exhibited the highest weight retention, losing a total of 11.4% or an
actual weight loss of 3.9% after 100 hours. The MEPPQ exhibited the
highest weight loss (72.5%) after 100 hours of 371°C (700°F). None of
the films exhibited good weight retention after 226 hours at 371°C (700°F)
in air.

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TABLE 4.   THERMAL CHARACTERIZATION OF POLYPHENYLQUINOXALINES

Polymer No.	Sample No. PH-1	Polymer	Film Thickness mm	Weight Loss (%) After Time (hr) at 316°C in air				Light Trans (%) After Time (hr) at 316°C in air			Flexibility Failure After Time (hr) at 316°C	
				25	403	1076	Act. Wt. Loss (1076)	0	403	1076		
3	106	LMW PPQ-I	.0508	5.7	6.8	15.6	9.9	58	23	0	>136	<403
5	105-2	IMW PPQ-II	.0356	6.1	6.6	8.6	2.5	68	48	32	>403	<1076
9	107-3	RaCo (1:3)	.0305	6.6	7.3	10.1	3.5	67	54	34	>403	<1076
12	110-3	BlCo (1:3)	.0432	6.9	7.5	9.5	2.6	63	46	28	>403	<1076

3.2   (Continued)

The aging study was conducted on films rather than powders because the measurements (flexibility and color) are more meaningful than a simple weight loss determination which is about all the powder samples would have offered. The measurement of retention of some mechanical properties such as film flexibility, is a better means of ascertaining the potential use life of a polymer at elevated temperature. A polymer in powder form can undergo significant   thermaloxidative degradation without exhibiting substantial weight loss due to a number of factors such as oxygen uptake, molecular weights of the degradation products too high to volatilize and/or crosslinking.

f.   Polymer Fusion (Flow) Tests

Polymer fusion tests were conducted to assist in assessing the processing capability of each polymer. These tests were performed on powdered samples of each polymer, prepared as follows:

A portion of the polymer solution was poured slowly into methanol in a Waring Blender. The resulting fibrous yellow polymer was isolated and boiled for 0.5 hour twice in methanol followed by treatment in the blender after each wash. Drying was accomplished at 130°C in vacuo for 4 hours. At this stage, the yellow solids exhibited a total weight loss of < 0.2% as determined by heating at 350°C for 1 hour under argon. The yellow solid was then pulverized in a Wig-L-Bug to a particle size of <60 mesh. Due to increased surface area and the environmental conditions, the powdered samples absorbed atmospheric water as indicated by an increase in total weight loss (1.5 to 2.0%) after 1 hour at 350°C in argon. Polymer fusion tests were performed on the powdered samples by sandwiching a small quantity of powder between aluminum foil and placing this in a preheated press under~200 psi for 10 minutes. As shown in

3.2   (Continued)

Table 3 the degree of fusion (processability) was ranked numerically
from 1 to 5, with 1 representing good fusion where the polymer essen-
tially melted in the center to form a tough translucent section while 5
represents poor fusion where no melting occurred but the powder
been pressed together. The intermediate molecular weight PPQ-II
(polymer No. 5) exhibited good fusion under the three different
temperatures while the low molecular weight form exhibited poor fusion
which is tentatively attributed to crosslinking inhibiting flow prior to
the formation of a good fusion disc. As indicated in Table 3, the
polymers which exhibited the best fusion from each of the four groups
of PPQ were low molecular weight PPQ-I (No. 3), intermediate
molecular weight PPQ-II (No. 5), random copolymer 1:3 (No. 9), and
block copolymer 1:3 (No. 12). It was known that PPQ-II generally
exhibits better processability than PPQ-I, hence it was not surprising
to observe better fusion in those copolymers containing a higher degree
of PPQ-II character.

g.   Solvent Compatibility Studies

Polymers No. 14 and 15 (Tables 2 and 3) were prepared, using starting
reactants from the same source in a 1:1 mixture of m-cresol and xylene and
in sym-tetrachloroethane (TCE), to determine if residual m-cresol has any
deterimental effect upon the thermaloxidative stability of the polymer and
also to observe if the handling characteristics of the TCE solution were
better. The solution viscosity of the two polymers (9000 and 14,000 cps)
as well as the η_{inh} (0.97 dl/g and 0.91 dl/g) were very similar. From poly-
mer No. 14, two films were prepared in the usual manner, one on the day the
polymer was prepared and the other, three days later. The two films from polymer
No. 14 and a film from polymer No. 15 were dried under essentially identi-
cal conditions. One of the films (prepared first) from polymer No. 14
exhibited weight loss of 6.82% after 1100 hours at 316°C (600°F) in circulat-
ing air while the other film (also No. 14) exhibited a high weight loss

3.2   (Continued)

(38.67%). In addition, the film from polymer No. 15 (made in TCE) which was also cast 3 days after polymer preparation, also exhibited relatively high weight loss (20.09%). The reason for the high weight loss is not known, but this necessitated the preparation of new films from solutions of polymers No. 3, 5, 9, and 12 for additional aging study to determine if solution shelf life had any determental effect upon the thermaloxidative behavior of the films. The repeated aging data as shown in Table 4, were very similar to that originally obtained, indicating the polymers have a stable shelf life. It should be noted that the film prepared from the polymer made in TCE (No. 15, Table 3) retained a higher percent of residual solvent and water (13.40%) than the film cast from the m-cresol-xylene polymer solution (No. 14, Table 3) based on actual weight loss measurements. Both films were dried under essentially identical conditions which suggests that TCE is more difficult to remove from this polymer under these drying conditions than to 1:1 mixture of m-cresol and xylene. To conclude, TCE did not offer any advantage over the m-cresol-xylene mixture as a solvent for PPQ in this preliminary study.

3.3   Fiber/Resin Compatibility Studies

Resin flow tests and graphite fiber wetting tests were conducted to generate a minimum quantity of composite-related information, which together with polymer thermal stability, would afford basis for ranking and selecting four candidate polymers for Task II.

3.3.1   Resin Flow Studies

Resin flow tests were conducted using the procedure detailed in Section 8.2.3 Appendix. The test under the heat and pressure conditions used, led to selection of seven polymers having good flow characteristics. Shown in Table 5 is a summary of salient resin flow test

TABLE 5   PARAMETERS AND RESULTS OF PPQ RESIN FLOW TESTS

Polymer No. [1]	Flow Test No.	Polymer Parameters Type	Tg °C (°F)	Prepreg Resin + Solvent % by Weight	Parameters Solvent Content % by Weight	Results Or Comments
16	13	PPQI	337 (638)	33.5	2.30	[3] (Selected)
2	8	PPQI	350 (662)	38.6	2.18	[2]
3	9	PPQI	335 (634)	31.8	5.58	[2]
4	12	PPQII	325 (616)	41.8	2.76	[3] (Selected)
5	7	PPQII	314 (597)	33.2	4.24	[3] (Selected)
7	11	3:1 Random copolymer	337 (638)	33.1	2.51	[2]
9	10	1:3 Random copolymer	325 (616)	36.8	2.69	[3] (Selected)
8	5	1:1 Random copolymer	335 (634)	37.0	2.92	[2]
11	1	1:1 Block copolymer	335 (634)	41.4	2.21	[2]
10	2	3:1 Block copolymer	352 (666)	33.3	2.90	[2]
12	3	1:3 Block copolymer	327 (620)	36.2	2.52	[3] (Selected)
17	6	2:3 Block copolymer	333 (631)	40.7	2.60	[3] (Selected)
13	4	MEPPQ	290 (554)	38.1	4.22	[3] (Selected)

[1]   Polymer numbers correspond to the same numbers cited in Table 2.

[2]   Significant prepreg interply adhesion was not obtained after the selected heat and pressure treatment of 316°C, 0.69×10^6 N/m^2, 15 min.

[3]   Complete prepreg interply adhesion was obtained after applying the selected heat and pressure treatment of 316°C, 0.69×10^6 N/m^2, 15 min.

3.3.1   (Continued)

parameters and results. The following polymers were selected: 1:3 random copolymer,
PPQ-II (two versions), PPQ-I, 1:3 block copolymer, 2:3 block copolymer, and MEPPQ.
Because the polymer systems and test conditions used did not yield measurable resin
flash off either around the prepreg's periphery or into the bleeder cloth, interply
adhesion between two prepreg layers was used as the primary criterion for resin flow.
Figure 7 shows the flow test specimen configuration.

3.3.2   Fiber Wetting Studies

The reasons for the wetting tests were: (1) to qualitatively determine if PPQ polymers
adhere readily to graphite, and (2) to determine and rank wetting and penetrating
capability of the different PPQ solutions into the graphite tows; each tow consisting
of approximately 10,000 filaments. Since the PPQ polymers are excellent film
formers, it was considered important that the polymer solutions penetrate into the
tows to provide thorough and complete wetting and not merely encapsulate the tows.

3.3.2.1   Single Fiber Wetting Studies

Single graphite fiber "wetting" studies were conducted using the thirteen polymer
systems listed in Table 2, and the procedure detailed in Paragraph 8.2. Scanning
electron photomicrographs were taken of the cross section of single (one to twenty)
fibers impregnated in thin polymer films which were stressed to failure. The photo-
micrographs are shown in Figures A-1 through A-5 (in Appendix).   Polymers 3, 5,
9, and 12 exhibited qualitatively good "wetting" (adherence) to the single graphite
fibers. As is evident in photographs A-1 through A-5, when good wetting (good
resin/fiber adherence) occurs, the fracture plane in the fiber and resin is in the
same locale with very little crack propagation along the resin/fiber interface (i.e.
Figure A-2). This is in contrast to the high incidence of fiber/resin debonding when
poor wetting occurs (i.e. Figure A-1).

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TWO PLYS OF AF 181 GLASS CLOTH

ONE PLY OF POROUS TFE/ GLASS CLOTH

TWO PLYS OF PREPREG (POLYMER/AF 181 CLOTH)

A-A (EXPLODED VIEW)
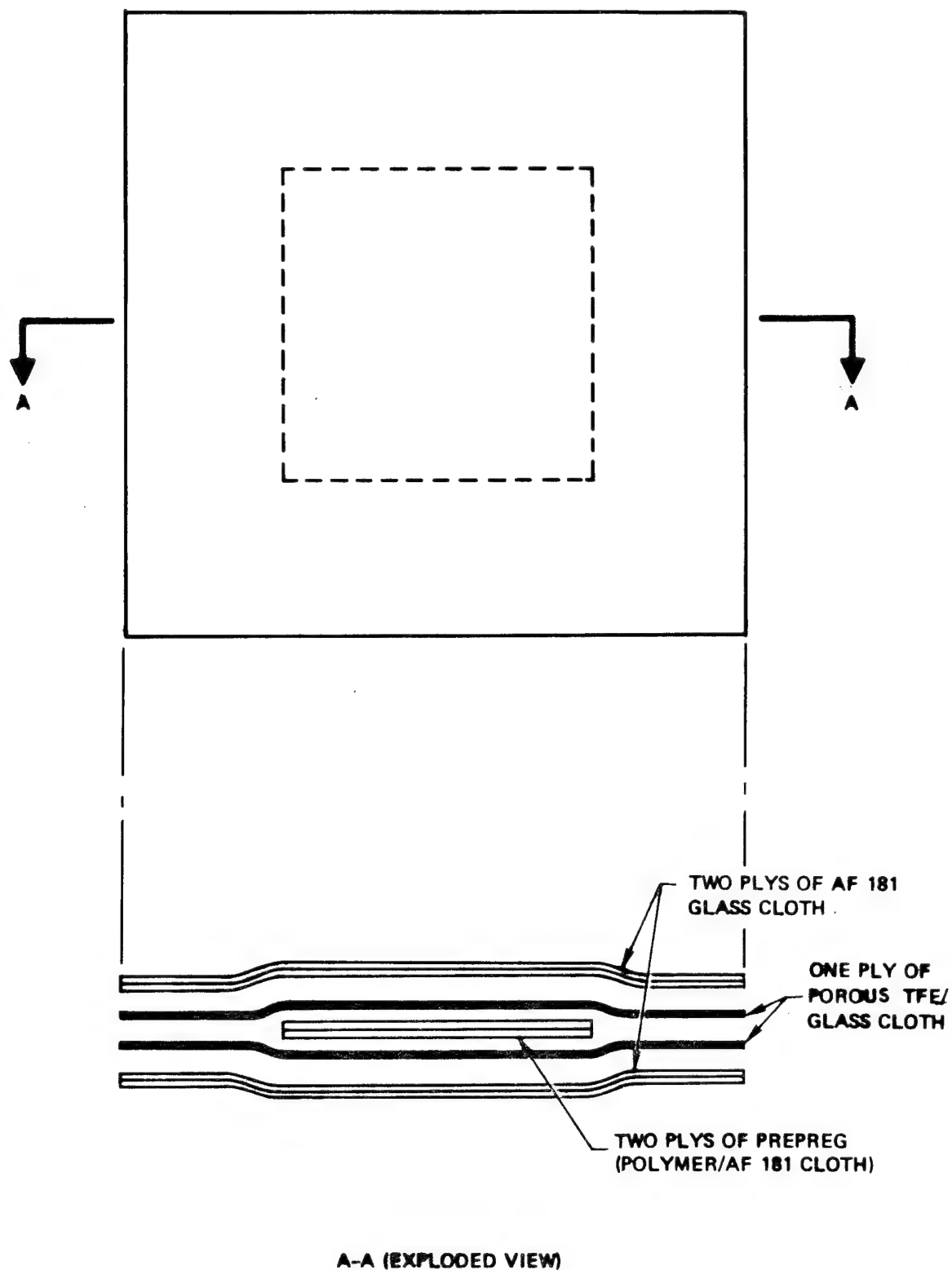
Figure 7   RESIN FLOW TEST SPECIMEN CONFIGURATION

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3.3.2.2 Graphite Tow Wetting Studies

Graphite tow wetting studies were also conducted using the thirteen polymers listed in Table 2. The test procedure used is detailed in Paragraph 8.2 Appendix. Resin ability for penetration and permeation into graphite tows was used as a measure of general wetting capability. Microscopic inspection and analysis of photoenlargement (~450X) of cross sections of resin-treated, dried tows were used to select resin systems of high penetration ability. Microscopic inspection, using a 40 power microscope led to selection of polymers No. 2, 3, 5, 9, 11, and 13. These polymers exhibited thorough wetting, rather than encapsulation of the graphite tows. The results of the tow wetting test were combined and polymers No. 2, 3, 5, 9, and 13 were finally selected. Figures A-6 through A-12 (in Appendix) are typical photoenlargements (450X) of dried tows treated with the polymers listed in Table 2. Figures A-6 and A-9 show examples of good and poor resin penetration respectively.

Four sets of conditions described in Paragraph 8.2 , were used in the graphite tow wetting study. In general, the combination of a low rate of fiber immersion into the polymer solution, and extended tow drying times resulted in more thorough penetration of resin into graphite tows. The 7 photoenlargements, Figures A-6 through A-12 (in Appendix A) are enlargements of composites made using the conditions designated Set A in Table A-1 , Paragraph 8.2 .

3.4 Final Polymer Selection – Task I

From Task I, the following four polymers were selected from the original thirteen for preliminary composite evaluation in Task II.

> PPQ-I Low Molecular Weight Version
> PPQ-II Intermediate Molecular Weight Version
> Random Copolymer (1:3)
> Block Copolymer (1:3)

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3.4   (Continued)

The selection was based on polymer characterization tests and fiber wetting and flow tests. The most important criteria for polymer selection were stability as determined in isothermal aging tests on films and processability as determined in fiber wetting and flow tests. The characterization and processing data indicated that PPQ-I, PPQ-II, and the random copolymer (1:3) should be selected. However, the processing studies (flow and wetting) showed that the fourth polymer should be MEPPQ (polymer No. 13) while the thermal stability studies rated this polymer last. Because of its low thermaloxidative stability, the MEPPQ was discarded and the next polymer on the list, the block copolymer (1:3) was chosen. Of the remaining polymers, it exhibited the best compromise in thermaloxidative stability and processability. The following section presents the information and data upon which this selection was based.

In the PPQ-I series, the high molecular version (No. 1, Table 2) was discarded early due to the high viscosity and/or gelling of the solution (even at 15% solids content). Although the intermediate molecular weight version (No. 2) exhibited a lower weight loss in isothermal aging than the low molecular weight version (4.6 vs. 7.5%), the latter version (No. 3) was selected primarily on the basis of better processability as indicated in pressure fusion and fiber wetting and flow tests.

In the PPQ-II series, the low molecular weight version (No. 6) provided a film which failed to exhibit the toughness of films from the other two versions. Of the remaining two polymers, the intermediate molecular weight version (No. 5) exhibited good performance in all of the tests and was selected over the high molecular weight version (No. 4) on the basis of film aging data and fiber wetting and flow tests.

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3.4   (Continued)

In the random and block copolymer series, the copolymers chosen were the 1:3 variation, consisting of a molar ratio of 1 part 3,3' -diaminobenzidine and 3 parts of 3,3', 4,4'- tetraaminobenzophenone to 4 parts of p-bis(phenylglyoxalyl) benzene. Again, the selection was made on the basis of overall performance in the characterization of fiber wetting and flow tests, with particular emphasis on the flow characteristics.

4.0 TASK II – PRELIMINARY COMPOSITE EVALUATION

The primary objective of Task II was to screen the four polymers from Task I and select the most promising polymer for more extensive evaluation in Task III. Task II was divided into two parts: Preliminary Composite Curing Studies and Preliminary Composite Testing. To accomplish the composite studies, the four polymers had to be synthesized in larger quantities and characterized. This permitted studies on polymer reproducibility.

It should be noted in reviewing the composite studies in Task II, that no attempt was made in this phase of the program to achieve maximum properties at elevated temperatures. The composites were not post cured and all tests were selected and intended for screening purposes only.

4.1 Polymer Synthesis and Characterization

The four selected polymers as shown in Table 6, were prepared on 0.4 mole scale (for polymer No. 16, 220g based upon reactants or 181g based upon polymer) using the procedures established in Task I and detailed in Section 6.1 Appendix. During the first synthesis of one of the four polymers, intermediate molecular weight PPQ-II, a clear orange solution with a viscosity of 5,400 cps was obtained. The synthesis was conducted on a 0.40 mole scale at 20% solids content in a 1:1 mixture of m-cresol and xylene at a stoichoimetric ratio of 0.985:1.000 (tetraamine to tetracarbonyl). In an attempt to increase the viscosity to more closely compare with that obtained for polymer No. 5, Table 2, additional tetraamine (1000g) was added. Upon stirring at ambient temperature for three days, the resulting solution became extremely viscous and partially gelled. The first synthesis was repeated to provide polymer No. 17, Table 6, having an η_{inh} of 1.05 dl/g to conform with the η_{inh} range specified for intermediate molecular weight PPQ-II. Characterization of the four polymers for Task II is given in Tables 6 and 7.

Although deviations in Brookfield solution viscosities were observed in comparing the properties of the four PPQ for Task II (Table 6) the overall properties compare favorably with those of the corresponding polymers in Task I (Table 2).

TABLE 6   CHARACTERIZATION OF POLYPHENYLQUINOXALINES FOR TASK II

| Polymer No. | Sample No. PH-1 | Polymer | Stoichiometry NH_2/CO | RX Scale (Mole) | Conc. % Solids [1] | Sol'n. Viscosity CPS After [2] | | η_{inh} dl/g | U. V. Spectral Data | |
						3 Days	11-14 Days		λ_{max}, mμ	ϵ
16	115	LMW PPQ-1	0.97/1.00	0.4	17.1	4,300	4,400	0.78	292	43785
17	114	IMW PPQ-II	0.985/1.000	0.4	20.0	5,000	5,700	1.05	282	57814
18	116	RaCo (1:3)	0.985/1.000	0.4	20.0	1,750	1,800	0.78	283	52713
19	117	BlCo (1:3)	0.985/1.000	0.4	18.4	17,000	17,000	1.31	283	52834
20	118	LMW PPQ-I	0.98/1.00	0.24	18.0	7,000	---	0.85	---	---
21	119	IMW PPQ-II	0.985/1.00	0.20	20.0	4,300	---	1.08	---	---

[1]   CONCENTRATION BASED UPON REACTANTS BY WEIGHT

[2]   BROOKFIELD VISCOSITY AT 25°C

4.1 (Continued)

The η_{inh} and ultraviolet spectroscopic data are in good agreement. The primary purpose of the ultraviolet spectral work was to check the reproducibility of the polymers. Based upon the characterization data of the four polymers in Task II, it appears as though good reproducibility was realized in scaling up from 0.05 mole to 0.40 mole. In addition, an extra batch each of low molecular weight PPQ-I and intermediate molecular weight PPQ-II were required for preliminary composite evaluation in Task II. These polymers (No. 20 and 21) whose characterization is also presented in Table 6 compared favorably with those previously prepared on a 0.40 mole scale, indicating good reproducibility.

The Tg of the PPQ as determined by DSD failed to agree consistently with those obtained by DSC even though both methods used the same heating rate (20°C/min) and atmosphere (nitrogen). In the DSD, a frequency sweep of 200 to 1000 cycles second was used with the Tg taken as the intercept of the temperature versus dissipation factor curve at 200 cycles/second. The Tg of the initial run should be lower than the Tg of the final run. However, as shown in Table 7, discrepancies occurred in the Tg values as determined by DSD, with the initial runs in two of the four polymers have Tg's higher than in the final runs. The reason for this is unknown, but problems were previously encountered in obtaining good reproducibility by DSD. Additional work could have been performed to alleviate these problems, but this effort would not have contributed significantly to the overall objective of the program. This was one of the reasons DSC was chosen for extensive Tg determinations rather than DSD.

The thermal transitions of these four polymers were also studied through dynamic mechanical relaxation measurements (DMRM) using a Vibron Viscoelastometer. As shown in Table 7, the temperature of the maximum dispersion peak is lower than the Tg obtained by DSC. However, the trend of the maximum dispersion peak temperatures is the same as that observed for the Tg's obtained by DSC. A

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TABLE 7. THERMAL CHARACTERIZATION OF POLYPHENYLQUINOXALINES FOR TASK II

Polymer No.	Glass Transition Temp., °C				Film Thickness, mm	Weight Loss (%) After Time (hr) at 315°C in air				Light Trans. (%) After Time (hr) at 315°C in air			Flexibility Failure After Time (hr) at 315°C	
	DSC [1]	DS D [2]		DMRM [3]		25	403	1076	Act. Wt. Loss	0	403	1076		
	Initial	Initial	Final											
16	351	360	354	337	.0508	4.9	6.2	11.0	6.1	62	26	5	>136	<403
17	318	380	330	290	.0965	7.4	8.4	11.9	4.5	59	15	4	>136	<403
18	311	339	351	285	.o737	8.5	9.5	14.0	4.5	59	23	3	>136	<403
19	326	364	324	307	.0787	6.6	7.7	11.9	5.2	61	23	6	>136	<403

[1] Differential Scanning Calorimetry, $\Delta T = 20°C/min$, N_2

[2] Dynamic Scanning Dielectrometry, $\Delta T = 20°C/min$, N_2, Tg taken as intercept of temperature versus dissipation factor curve at 200 cycles/second.

[3] Dynamic Mechanical Relaxation Measurements, $\Delta T = 10°C/min$, N_2, temperature reported is that of Maximum Dispersion Peak at 110 cycles/second.

4.1   (Continued)

representative curve of the dynamic dielectric   relaxation spectrum of one of the
four polymers (LMW-PPQ-I, polymer No. 16) is shown in Figure 8.

As shown in Table 7, films of the four polymers for Task II exhibited good aging
performance at 316°C in air. The initial weight loss which occurred during the
first 25 hours in attributed to residual solvent and/or water. The actual weight
loss after 1076 hours at 316°C in circulating air represents the difference between
the weight loss after 25 and 1076 hours. The actual weight losses after 1075 at
316°C varied from 4.5 to 6.1%. The retention of film flexibility after aging at
316°C was less than previously measured for similar polymers (No. 3, 5, 9, and 12,
Table 3) prepared on a smaller scale. However, this may be partially attributed
to increased film thickness.

4.2   Preliminary Composites Curing Studies

Effects of individual composite cure parameters on laminate properties were
investigated using a two-level experimental approach. Composite cure temperature,
pressure, and duration of cure were varied with four sets of six laminates being
prepared from each of the four polymers. Table 8 lists details of individual pre-
pregs, cure parameters used and the final test results. Composite fabrication
details are given in Section 8.0 Appendix.

In selecting the cure parameters, the glass transition temperature of each polymer
was used as the lower level cure temperature. Temperatures of 10°C (18°F) above
the glass transition points were used as upper level cure temperatures. Cure
temperatures near the Tg of each polymer were specifically selected to isolate
postcuring effects on laminate properties at elevated temperatures. (Postcuring
studies and the effects of postcure on laminate strength at elevated temperatures,
were conducted in Task III). Laminate pressures were intentionally held to a maximum
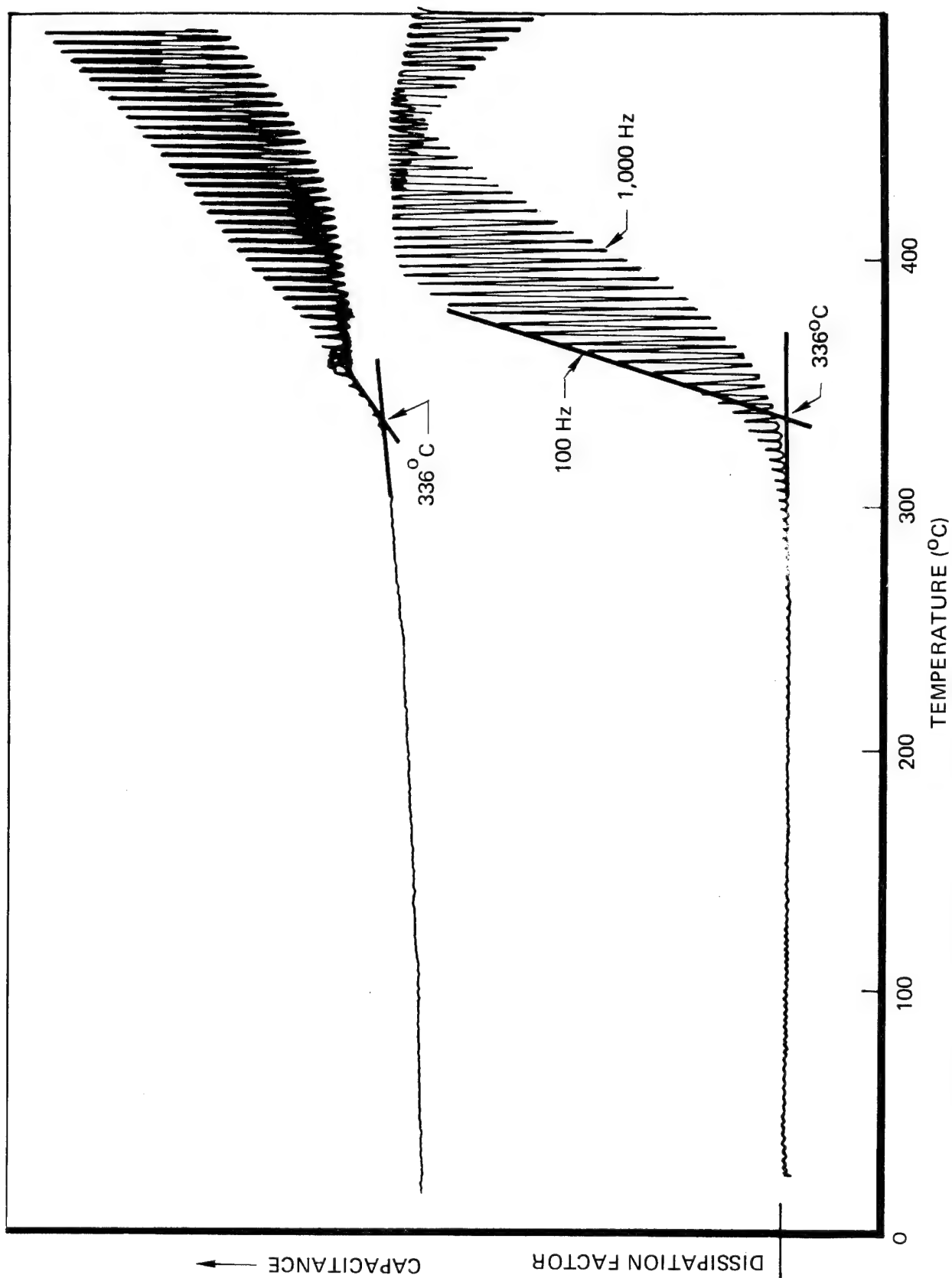
Figure 8 : DYNAMIC DIELECTRIC RELAXATION SPECTRUM OF PPQ–1 (IN NITROGEN)

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TABLE 8 PRELIMINARY COMPOSITE CURE PARAMETERS

Spec. No.	Polymer	Prepreg Solvent Content	Press Cure Parameters Temperature/Duration/Pressure °C/Min/N/m²	°F/Min/psi	% Resin Content [4]	% Void Content [5]	Specific Gravity	Collimation	Interlaminar Shear N/m² [10]	psi [11]
1	RaCo (1:3)	11%	310/30/0.69 × 10⁶ [1]	590/30/100	50	8.2	1.45	Good	36.6 × 10⁶	5310
2	RaCo (1:3)	11%	310/60/0.69 × 10⁶	590/60/100	50	5.9	1.49		45.7	6630
3	RaCo (1:3)	11%	322/30/0.69 × 10⁶ [2]	612/30/100	50	0.2	1.58		45.7	6630
4	RaCo (1:3)	11%	322/60/0.69 × 10⁶	612/60/100	50	8.4	1.49		43.2	6270
5	RaCo (1:3)	11%	310/60/1.38 × 10⁶	590/60/200	50	4.7	1.52		41.8	6060
6	RaCo (1:3)	11%	322/60/1.38 × 10⁶	612/60/200	50	2.7	1.64	Good	44.5	6450
7	BICo (1:3)	10%	326/30/0.69 × 10⁶ [3]	618/30/100	50	9.3	1.44	Good	29.8	4320
8	BICo (1:3)	10%	326/60/0.69 × 10⁶	618/60/100	50	10.6	1.41		28.7	4170
9	BICo (1:3)	10%	336/30/0.69 × 10⁶	636/30/100	50	8.6	1.44		38.9	5640
10	BICo (1:3)	10%	336/30/0.69 × 10⁶	636/30/100	50	12.5	1.38		33.1	4800
11	BICo (1:3)	10%	326/60/1.38 × 10⁶	618/60/200	50	9.6	1.43		38.7	5610
12	BICo (1:3)	10%	336/60/1.38 × 10⁶	636/60/200	50	13.6	1.37	Good.	46.1	6690
13	PPQ1	30%	351/30/0.69 × 10⁶ [6]	664/39/100	50	24.9	1.19	Good	26.3 × 10⁶	3810
14	PPQ1	10%	351/60/0.69 × 10⁶	664/60/100	50	23.0	1.42		20.6	2990
15	PPQ1	10%	361/60/0.69 × 10⁶ [7]	682/30/100	50	28.2	1.14		19.2	2790
16	PPQ1	10%	361/60/0.69 × 10⁶	682/60/100	50	18.4	1.30		24.2	3510
17	PPQ1	10%	351/60/1.38 × 10⁶	664/60/200	50	18.0	1.30		30.4	4410
18	PPQ1	10%	361/60/1.38 × 10⁶	682/60/200	50	16.1	1.33	Good	29.2	4230
19	PPQ2	44%	318/30/0.69 × 10⁶ [8]	604/30/100	50	10.3	1.44	Good	35.2	5100
20	PPQ2	30%	318/30/0.69 × 10⁶	604/60/100	50	10.9	1.42		41.0	5940
21	PPQ2	30%	328/30/0.69 × 10⁶ [9]	622/30/100	50	12.5	1.40		32.9	4770
22	PPQ2	30%	329/60/0.69 × 10⁶	622/60/100	50	9.8	1.44		38.7	5610
23	PPQ2	30%	318/60/1.38 × 10⁶	604/60/200	50	9.8	1.44		46.3	6720
24	PPQ2	30%	328/60/1.38 × 10⁶	622/60/200	50	9.7	1.46	Good	39.7	5760

△1 RaCo (1:3) Tg = 310°C (590°F)

△2 Tg + 10°C

△3 BICo(1:3) Tg = 326°C (618°F)

△4 Negligible resin flow occurred during laminate cure

△5 Based on 50% resin content and ideal laminate density, that is $\left(\rho_{ideal} - \rho_{measured} \right) \div \rho_{ideal}$

△6 PPQ1 Tg = 351°C (664°F)

△7 Tg + 10°C

△8 PPQ2 Tg = 318°C (604°F)

△9 Tg + 10°C

△10 Average of 3 specimens

△11 Specimen configuration .25 cm × .63 cm × 1.77 cm, L/D ratio = 5

△12 Selected preliminary cure schedules

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4.2   (Continued)

of 1.38×10^6 N/m^2 (200 psi) to stay within the limits of SOA autoclaves, should this technology be extended to component fabrication.

The cure schedules used to prepare laminates 3, 12, 17, and 23 (Table 8) were selected as the best optimum preliminary cure for each of the four polymers, and used to prepare the laminates for the Task IIB studies. High interlamdnar shear strength (ILS) at room temperature was the first criterion for selecting the above preliminary cure schedules and the absence of voids was used as the second criterion. Figures 9 through 12 are cross section photoenlargements of laminates 1 through 24, Table 8. As evident from the photoenlargements, laminates 3, 12, 17, and 23 displayed the least amount of voids. The void contents listed in Table 8 are theoretical void contents, computed from the composite and constituents densities and fiber volume. Examination of the cross section photoenlargements, Figures 9 through 12, reveal in many cases, high void contents, but none appear over 12-15%, indicating that the computed theoretical values are in error and obviously too high. Laminates 3, 12, 17, and 23 have void contents estimated at 2% based on analysis of higher magnification photoenlargements of the laminates cross section and are within acceptable limits. The good strength values, obtained under Task IIB, and described later in this report, also support the above conclusion.

Scanning electron photomicrographs (SEM) of all laminates listed in Table 8 were made and analyzed. Figures A-13 through A-16 (in Appendix) are SEM of inter-laminar shear ILS test speciments of laminates 3, 12, 17, and 23 taken after testing. These photographs are typical, representative of views normal to fiber longitudinal axis near location of load failure area. Note the degree of resin to fiber adherence in the photos. It is evident from these studies that the ILS stength can be improved with better fiber to resin bond, consequently the reported ILS values are conservative and should improve.

It should be noted that the highest ILS values for BlCo(1:3), PPQ-I and PPQ-II derived laminates were obtained from composites made under a pressure of 1.38×10^6 N/m^2 (200 psi). A pressure of 0.69×10^6 N/m^2 (100 psi) was sufficient to produce high ILS values for RaCo(1:3) derived laminates. As related to prepreg solvent
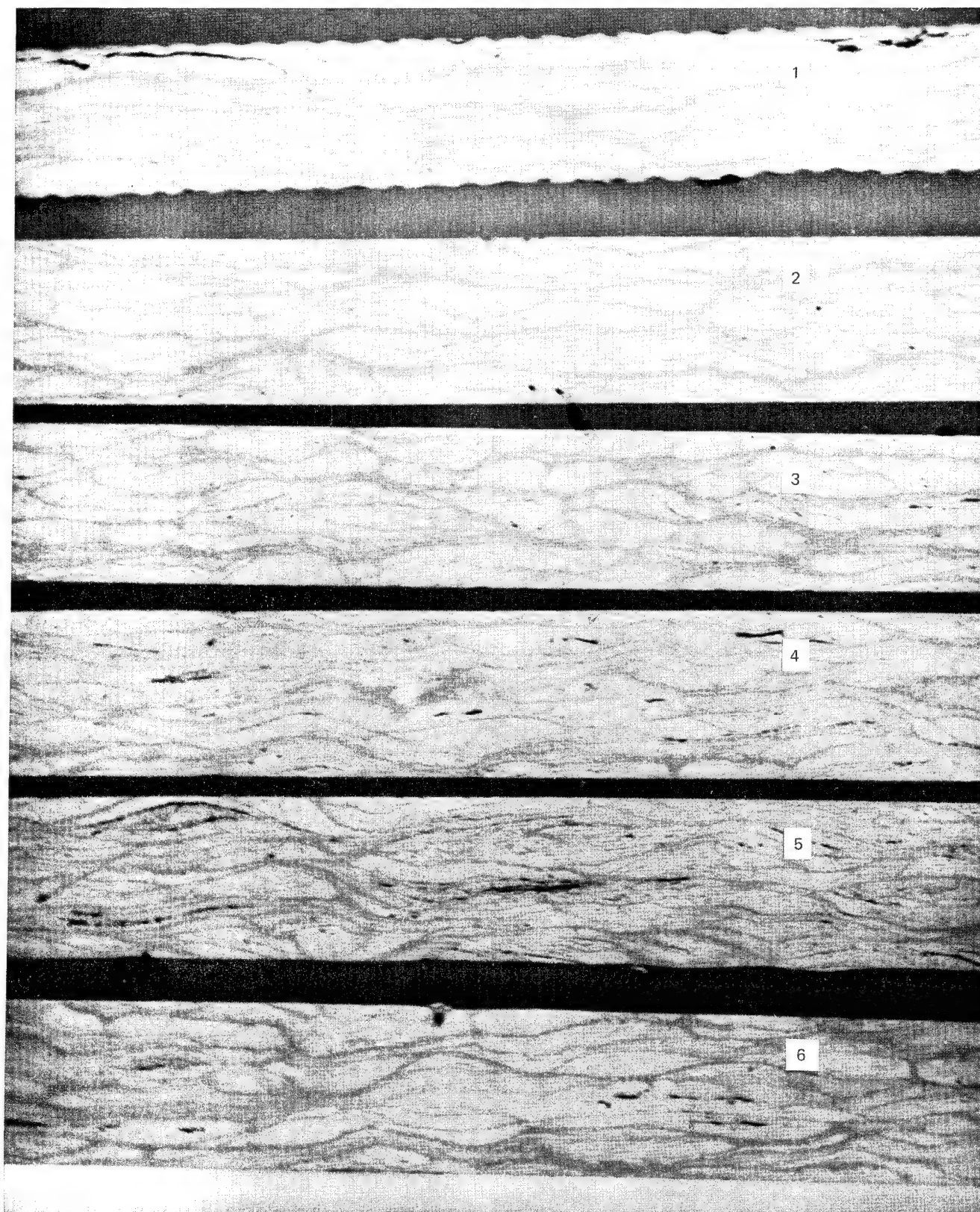
Figure 9:   CROSS SECTION PHOTO ENLARGEMENTS OF LAMINATES
1 THROUGH 6 (TABLE 8). X 10

Figure 10: CROSS SECTION PHOTO ENLARGEMENTS OF
LAMINATES 7 THROUGH 12 (TABLE 8) . X 10
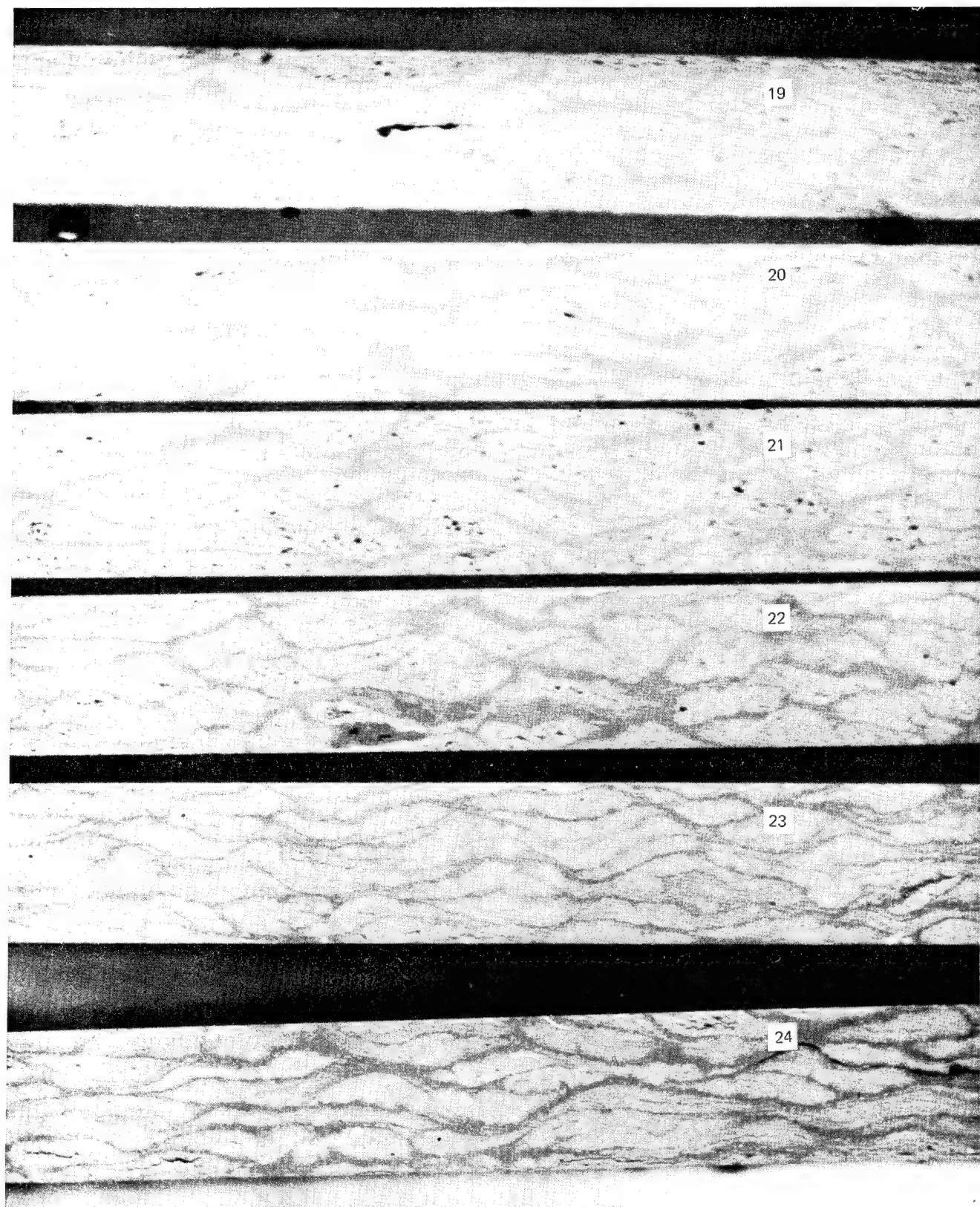
Figure 11: CROSS SECTION PHOTO ENLARGEMENTS OF
LAMINATES 13 THROUGH 18 (TABLE 8). X 10

Figure 12: CROSS SECTION PHOTO ENLARGEMENTS OF
LAMINATES 19 THROUGH 24 (TABLE 8). X 10

4.2 (Continued)

content, those prepregs containing the higher content (10-15%) listed in Table 8, had considerable flexibility at room temperature, thus showing promise of being amenable to fabrication of laminates on nonplanar or complex shapes. Prepregs with less than 5% solvent content were very brittle and care had to be taken to prevent damage to the fiber during handling and processing. A prepreg of this nature would be difficult to use in component fabrication and, therefore, attempts were made to maintain a reasonable degree of flexibility (high solvent content) in this prepreg.

4.3 Preliminary Composite Testing

4.3.1 Mechanical Property Tests

Unidirectional composites were fabricated using the cure parameters selected above for the block, random, PPQ-I and PPQ-II Polymers. The laminates were tested for ILS, tensile, and flexural strength at 21°C (70°F), 204°C(400°F) and 316°C(600°F). The test results are tabulated in Table 9 through Table 11 and summarized in Figure 13 through Figure 15. Tensile and flexural moduli are summarized in Figures 16 and 17. At 316°C (600°F), all values were low, as expected. This is attributed to theromplastic flow of the resins at 316°C (600°F) resulting from not postcuring the test panel. Inspection of the flexural specimens tested at 316°C(600°F) revealed a deformation in a manner characteristic to resin thermoplastic flow. The 21°C (70°F) strength values are competitive with HMS graphite/epoxy systems, Figures 14 and 15 indicating good composite potential. It is significant that the composite strengths, even with no postcure, show little decline at 204°C (400°F).

4.3.2 Isothermal Aging Studies

Four laminates, one from each polymer, were aged 500 hours at 371°C (700°F) after having been prepared using the procedures of paragraph 8.2.6 and the preliminary cure schedules selected above. The results of the ITGA tests are summarized in Table 12. At the end of the 500 hours aging period, very little resin matrix could be observed on the specimens, the yield being mostly graphite filaments. The weight loss values listed in Table 12 include partial

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TABLE 9. SHORT BEAM INTERLAMINAR SHEAR STRENGTH OF COMPOSITES MADE WITH SELECTED CURE SCHEDULES

Item No.	Polymer	Interlaminar Shear Strength				[1] [2]	
		21°C (70°F)		204°C (400°F)		316°C (600°F)	
		N/m^2	psi	N/m^2	psi	N/m^2	psi
1	Ra Co	40.1×10^6	5,942	19.3×10^6	2,795	1.7×10^6	252
2	BI Co	$33.3 \times$	(4824) [3]	$29.9 \times$	4,329	$0.9 \times$	132
3	PPQI	$24.0 \times$	3,488	$24.0 \times$	3,492	$2.0 \times$	296
4	PPQII	$36.6 \times$	5,302	$25.4 \times$	3,686	$2.1 \times$	306

[1] Without Postcure

[2] Average of 3 tests unless specified

[3] This value represents an average of two test results, the third test yielded an ILS value of 1647 psi and it was excluded from the calculation

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TABLE 10. TENSILE STRENGTH OF COMPOSITES MADE WITH SELECTED CURE SCHEDULES

Item No.	Polymer	Tensile Strength					
		21°C (70°F)		204°C (400°F)		316°C (600°F) △1 △2	
		N/m^2	psi	N/m^2	psi	N/m^2	psi
1	RaCo	7.4×10^8	107,300	5.6×10^8	81,400	4.1×10^8	59,700
2	BICo	$7.2 \times$	104,300	$6.1 \times$	88,300	$6.1 \times$	88,700
3	PPQ1	$4.1 \times$	59,300	$3.7 \times$	54,400	$2.8 \times$	41,400
4	PPQ2	$6.4 \times$	92,300	$6.3 \times$	91,600	$5.0 \times$	72,200

△1 - Without Postcure

△2 - Average of 5 Tests

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TABLE 11.   FLEXURAL STRENGTH OF COMPOSITES MADE WITH SELECTED CURE SCHEDULES

Item No.	Polymer	Flexural Strength					
		21°C (70°F) [1]		204°C (400°F) [1]		316°C (600°F) [2]	
		N/m^2	psi	N/m^2	psi	N/m^2	psi
1	RaCo	7.3×10^8	105,300	5.2×10^8	75,600	$.13 \times 10^8$	1,914
2	BICo	6.7 x	96,800	6.1 x	88,700	.47 x	6,648
3	PPQ1	5.9 x	85,500	5.4 x	77,700	2.1 x	30,400
4	PPQ2	6.1 x	88,300	5.6 x	80,700	.53 x	7,650

[1] Without Postcure

[2] Values are average of 3 tests.

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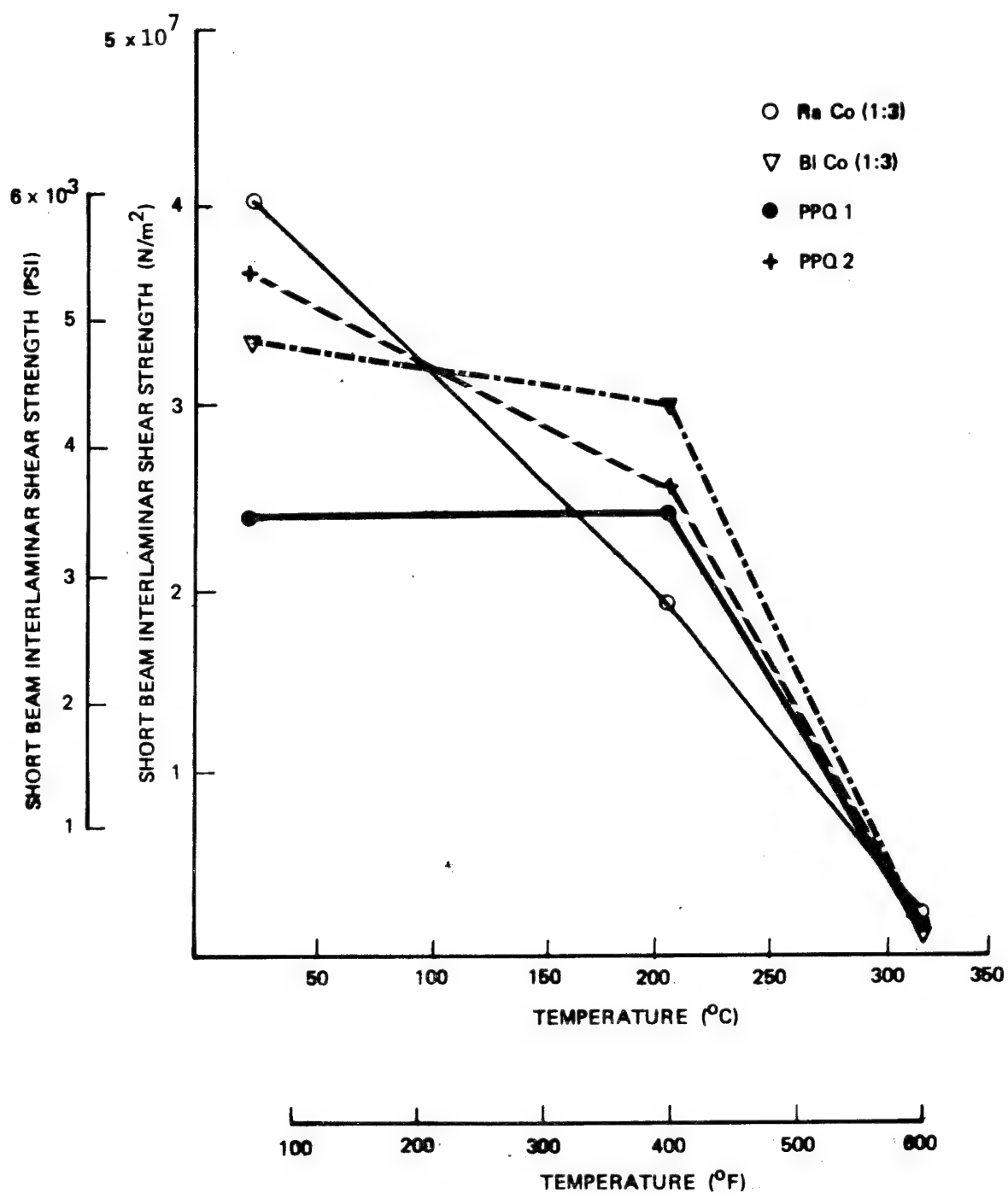
Figure 13: SHORT BEAM ILS OF COMPOSITES MADE WITH THE FOUR
CANDIDATE POLYMERS (WITHOUT POSTCURE)

49
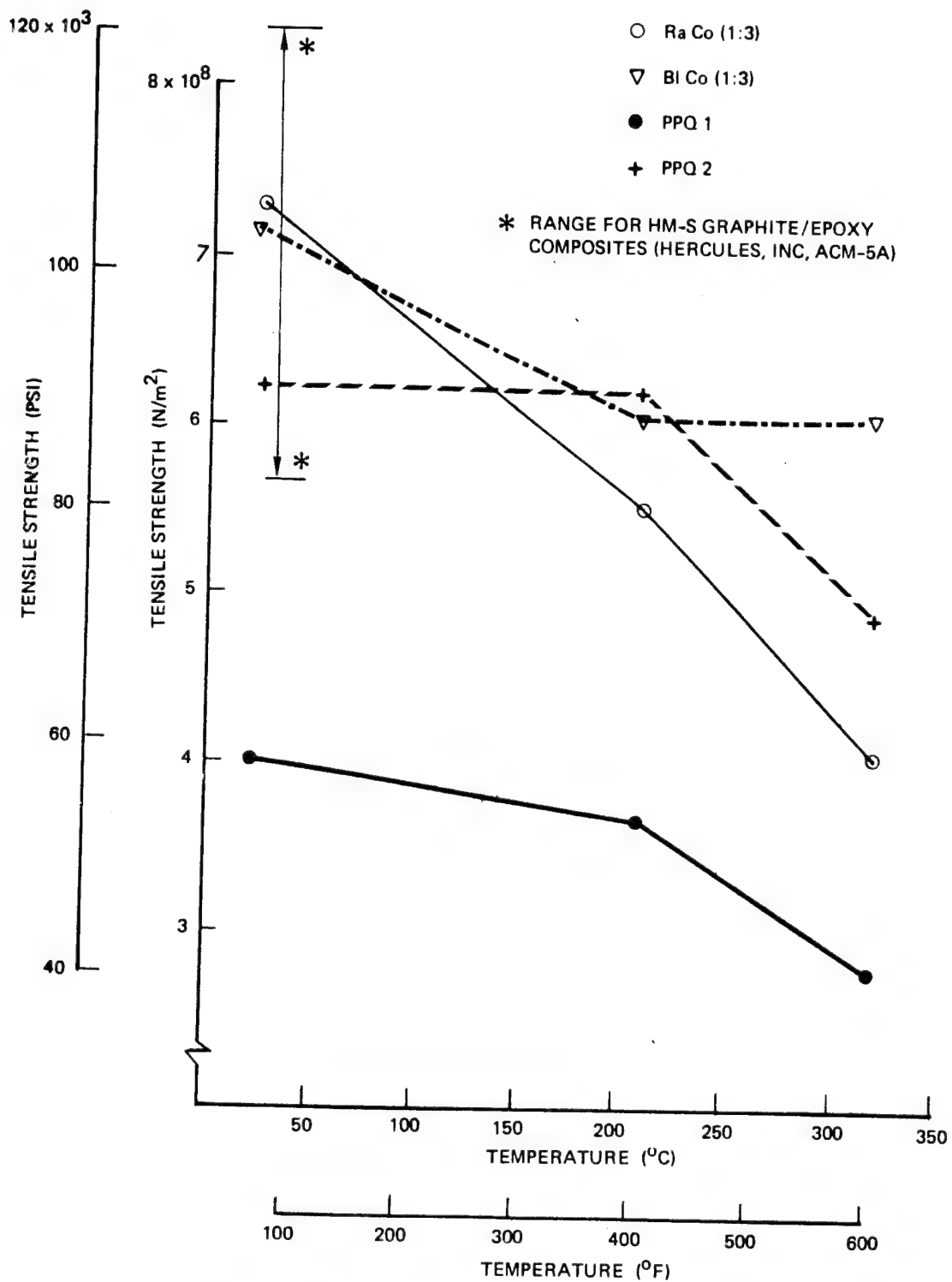
Figure 14: TENSILE STRENGTH OF COMPOSITES MADE WITH THE FOUR CANDIDATE POLYMERS (WITHOUT POSTCURE)

50
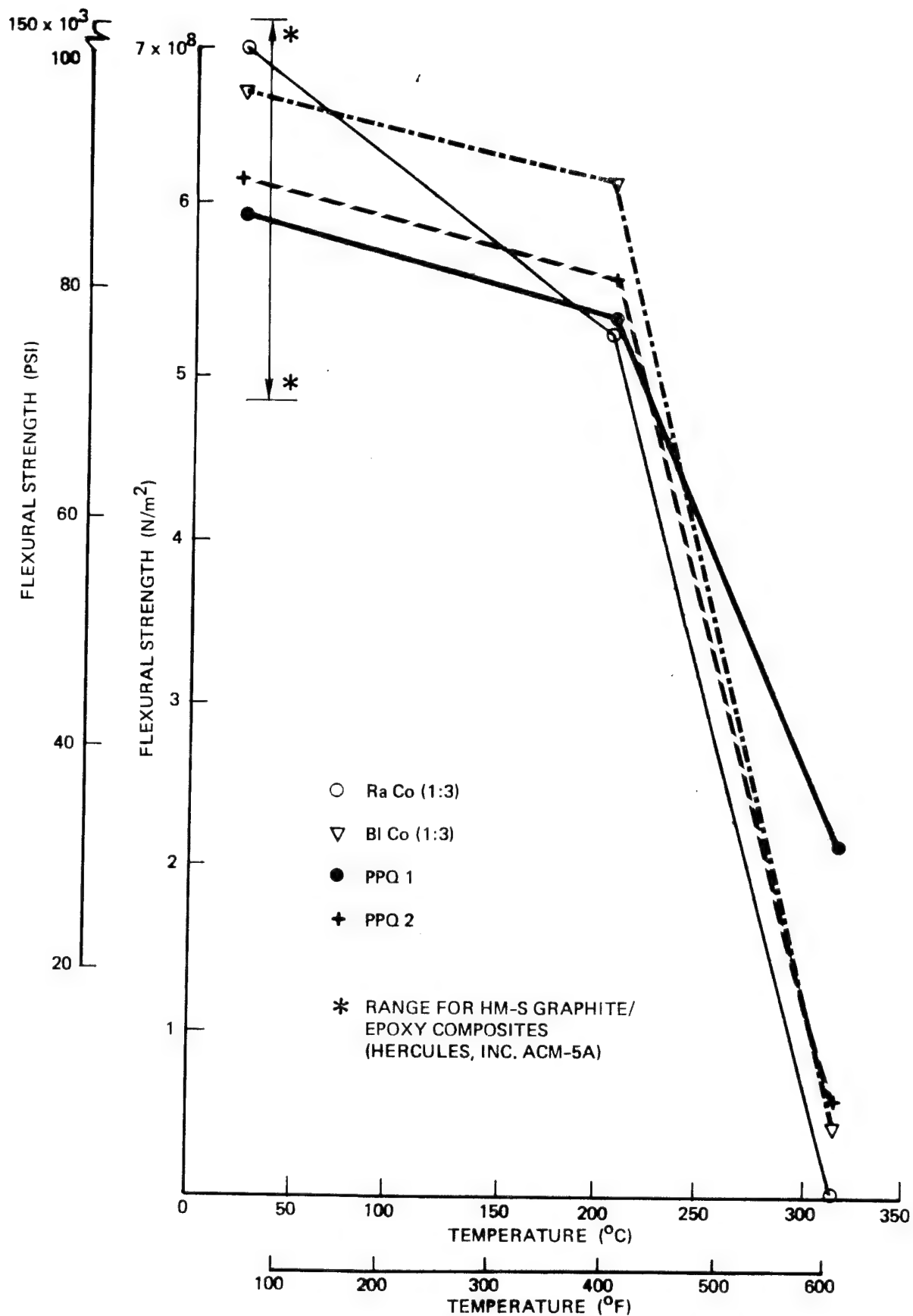
Figure 15: FLEXURAL STRENGTH OF COMPOSITES MADE WITH THE FOUR
CANDIDATE POLYMERS (WITHOUT POSTCURE)

51
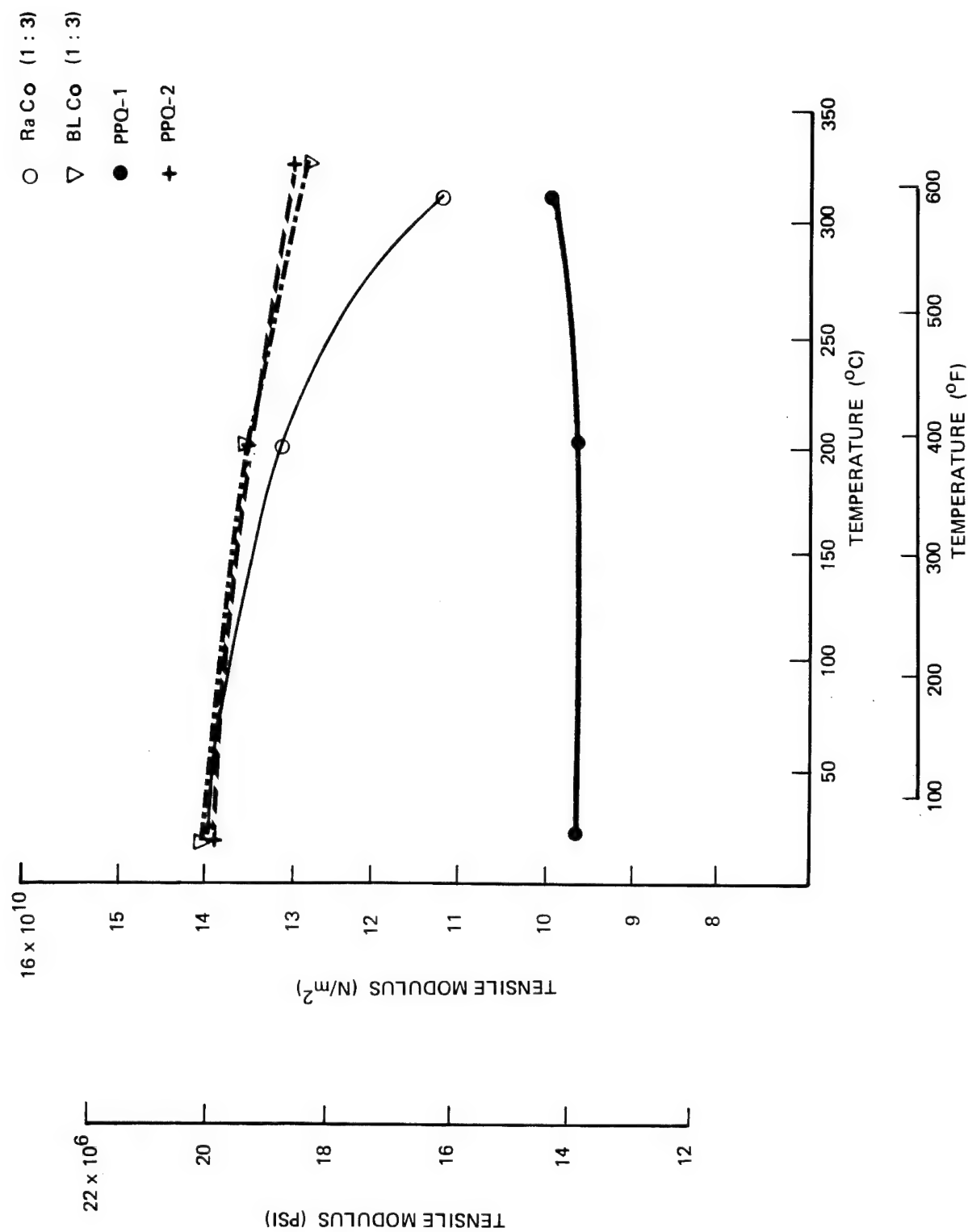
Figure 16: TENSILE MODULUS VS TEMPERATURE FOR UNIDIRECTIONAL PPQ/GRAPHITE COMPOSITES (WITHOUT POSTCURE)
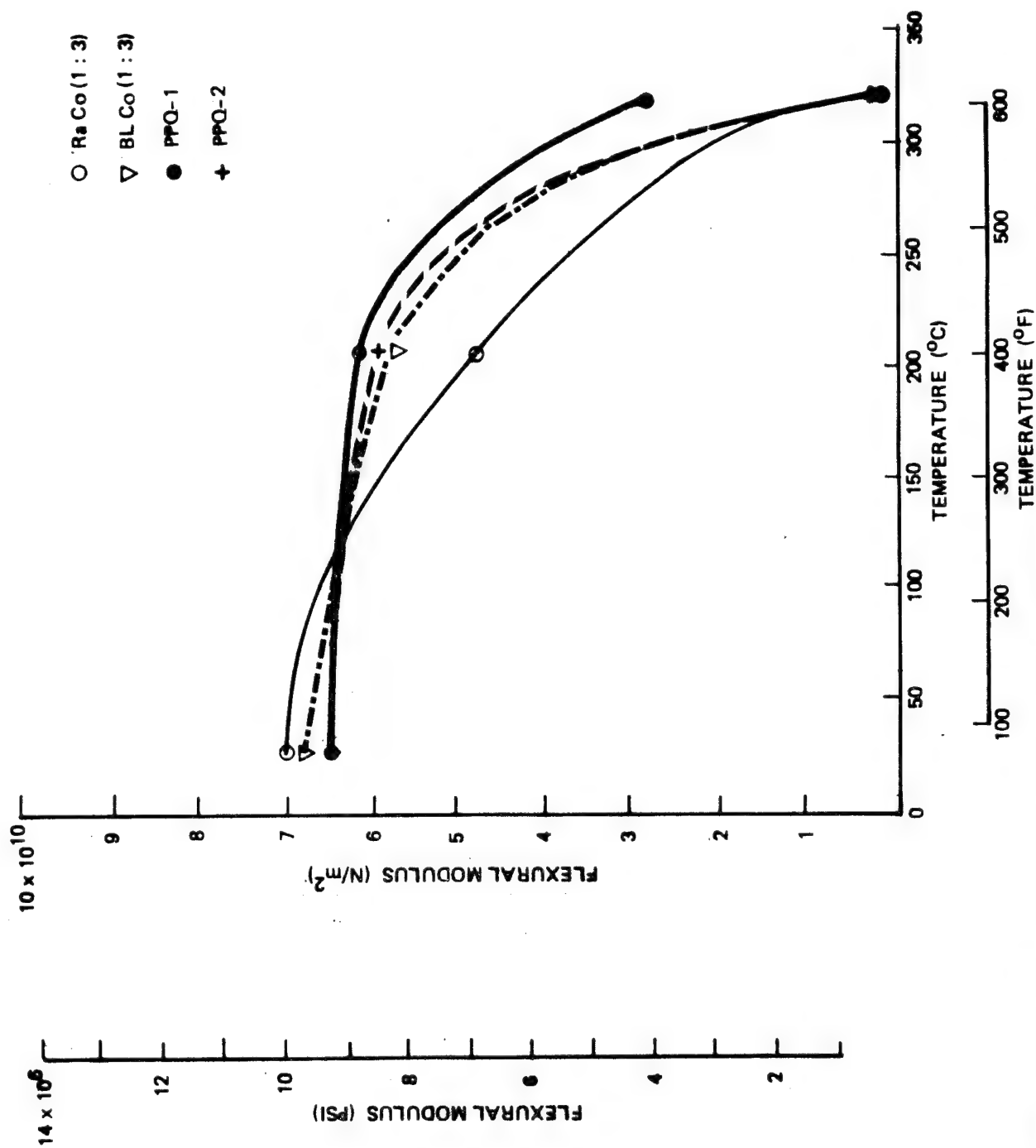
Figure 17: FLEXURAL MODULUS VS TEMPERATURE FOR UNIDIRECTIONAL PPQ/GRAPHITE COMPOSITES (WITHOUT POSTCURE)

TABLE 12 ELEVATED TEMPERATURE 371°C (700°F) AGING OF TASK II COMPOSITES

Item No.	Polymer	Weight Loss (%)		
		72 hrs.	Aging Time 250 hrs.	500 hrs.
1	Ra Co (1:3)	3.8	29	52
2	Bl Co (1:3)	3.7	29	55
3	PPQ 1	5.0	20	49
4	PPQ 2	4.9	38	55

TABLE 13 SPECIFIC GRAVITY OF TASK II POLYMERS AND TASK II COMPOSITES

Item No.	Polymer Type	Polymer [1]▷ Sp Gr 22°C (72°F)	Composites [2]▷ Sp Gr 22°C (72°F)
1	Ra Co (1:3)	1.22	1.49
2	Bl Co (1:3)	1.22	1.41
3	PPQ 1	1.24	1.34
4	PPQ 2	1.26	1.39

[1]▷ Densities were determined by pycnometry using cast films of each polymer. Prior to measurements, all films were prebaked at 315°C for 24 hours to drive off residual solvents.

[2]▷ Calculated from weight/volume measurements in air.

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4.3.2 (Continued)

fiber weight loss due to oxidation of the exposed filaments. These results indicate that 371°C (700°F) is an excessively high heat environment for prolonged exposure of the four polymers evaluated. Weight loss up to 72 hours is relatively low and the laminates should retain usable structural properties for these short periods of time at 371°C.

4.3.3 Specific Gravity of Task II Composites and Matrix Polymers

The specific gravity of laminates made in Task IIB was determined and the values are listed in Table 13.

The densities of each of the four polymers selected for Task II were determined and these values are listed in Table 13.

4.3.4 Polymer Coefficient of Thermal Expansion

The coefficient of thermal expansion was determined in the temperature range of -196°C (-320°F) to 316°C (600°F). Table 14 lists average coefficient values for the entire range and for specific materials within the range. The effect of elevated test specimen cure temperature on the coefficient of thermal expansion of the random copolymer (1:3) was determined. Excepting the 23°C(75°F) to 65°C(150°F) temperature range, increasing the cure temperature of the random copolymer test specimen from 322°C(612°F) to 399°C(750°F) increased the coefficient of thermal expansion. This indicates small increases in thermal expansion can be expected in postcured composites. However, with exception of PPQ-II, the polymers had essentially equivalent thermal expansions over the range studied. PPQ-II was approximately a factor of 2 higher.

4.4 Polymer Selection for Task III

The block copolymer (1:3) was selected for Task III. The selection was based on the polymer's weight retention on aging at 316°C (600°F), room temperature tensile and flexural properties, and retention of these properties at elevated temperatures.

TABLE 14 COEFFICIENT OF THERMAL EXPANSION OF TASK II POLYMERS

Polymer	Temperature Range								Cure Parameters
	△1 -196° to 316°C (-320° to 600°F)		△2 -196° to 79°C (-320° to 175°F)		△2 24° to 66°C (75° to 150°F)		△2 66° to 316°C (150° to 600°F)		
	mm/mm/°C	(in/in/°F)	mm/mm/°C	(in/in/°F)	mm/mm/°C	(in/in/°F)	mm/mm/°C	(in/in/°F)	
PPQI	6.16×10^{-5}	3.42×10^{-5}	3.44×10^{-5}	1.91×10^{-5}	5.35×10^{-5}	2.97×10^{-5}	8.17×10^{-5}	4.54×10^{-5}	361°C (682°F)
PPQ II	9.48 x	5.27 x	4.52 x	2.51 x	6.23 x	3.46 x	14.16 x	7.87 x	328°C (622°F)
Ra Co	5.09 x	2.83 x	4.39 x	2.44 x	4.39 x	2.44 x	5.60 x	3.11 x	399°C (750°F)
BI Co	4.66 x	2.59 x	3.40 x	1.89 x	5.18 x	2.88 x	6.12 x	3.04 x	322°C (612°F)
BI Co	5.29	2.94 x	4.59 x	2.55 x	4.46 x	2.48 x	6.32 x	3.51 x	336°C (636°F)

△1 Represents average coefficient over the entire temperature range of -196 to 316°C (-320 to 600°F)

△2 Values based on average slope of expansion curve within the temperature ranges indicated.

5.0 TASK III - ADVANCED COMPOSITE EVALUATION

The objective of this task was to conduct detailed characterization tests on advanced composites made from the polymer selected in the previous Task; namely PPQ block copolymer (1:3). Task III composite work was divided into two parts: Postcure Studies and Advanced Composite Evaluation. To accomplish this work, additional quantities of BICo (1:3) were synthesized and characterized. Table 15 shows the results of the synthesis characterization tests performed on these polymers. Comparison of this data with that previously obtained in Tasks I and II reveal good reproducibility in the synthesis process.

5.1 Postcure Studies

A study was conducted to increase the heat resistance of block copolymer (1:3) composites by postcuring laminates at temperatures between 371°C (700°F) and 454°C (850°F). The study led to selection of postcure schedule consisting of 454°C (850°F) and $1.4 \times 10^6 N/m^2$ (200 psi) pressure for 1 hour in addition to the cure schedule selected in the previous Task. The postcure schedule selection was based on the approach described below:

Test laminates were prepared using five different preliminary postcure schedules. The laminates were briefly characterized in terms of flexural strength and modulus at 22°C (71°F) and 316°C (600°F). The test results, summarized in Table 16, were used to select three additional laminate postcure schedules for further study. The flexure test results listed in Table 16 suggested selection of the postcure schedules listed below:

1. 2 hours at 399°C (750°F) under $1.4 \times 10^6 N/m^2$ (200 psi)
2. 1 hour at 427°C (800°F) under $1.4 \times 10^6 N/m^2$ (200 psi)
3. 1 hour at 454°C (850°F) under $1.4 \times 10^6 N/m^2$ (200 psi)

The postcure temperature of 454°C (in schedule 3) was an arbitrary selection. The selection is biased by the trend observed in the preliminary postcure study results where progressively higher postcure temperatures yielded higher flexure strength and moduli at 316°C (600°F).

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TABLE 15. CHARACTERIZATION OF THE PHENYLQUINOXALINE BLOCK COPOLYMER (1:3) FOR TASK III

Polymer No.	Sample No. PH-1	Stoichiometry* NH₂/CO	Rx Scale (Mole)	Conc.,* % Solids	Sol'n Viscosity* cps After		η_inh,* dl/g	U.V. Spectral Data*	
					3 Days	11 Days		λ_max, mu	ε
22	148	0.985/1.000	0.40	18.6	22,150	23,000	1.46	283	49,759
23	152	0.985/1.000	1.00	18.1	20,800	--	1.66	283	49,844
24	158	0.985/1.000	1.00	18.3	21,400	--	1.61	283	49,963

*Defined in Table 2

Polymer No.	Glass Transition Temp., °C		Film Thickness, mm	Weight Loss (%) after Time (Hr.) at 316°C in air				Light Trans. (%) After Time (Hr.) at 316°C in air			Flexibility Failure After Time (Hr.) at 316°C
	DSC [1]	DMRM [2]		24	377	1076	Act. Wt. Loss	0	377	1076	
22	320	304	.0533	5.6	7.4	11.0	5.4	81	61	25	>377 <1076
23	318	303	.0686	6.1	7.2	11.2	5.1	79	58	24	>377 <1076
24	322	306	.0584	5.6	7.1	10.2	4.6	83	60	32	>377 <1076

[1] Differential Scanning Calorimetry, ΔT = 20°C/min,N₂

[2] Dynamic Mechanical Relaxation Measurements, ΔT=10°C/min, N₂, temperature reported is that of Maximum Dispersion Peak at 110 cycles/second.

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TABLE 16. FLEXURAL PROPERTIES OF Bi Co (1:3) DERIVED LAMINATES POSTCURED USING PRELIMINARY POSTCURES

ITEM NO.	CURE/ POSTCURE CONDITIONS [1]	STRENGTH, N/m² (psi)				MODULUS, N/m² (psi) [2]			
		21°C (71°F)		316°C (600°F)		21°C (71°F)		316°C (600°F)	
1-1	[3]	--	--	3.2×10^8	(46,000)	--	--	--	--
1-2	↕	--	--	3.6×10^8	(52,000)	--	--	2.8×10^{10}	(4.0×10^6)
1-3		--	--	4.0×10^8	(58,000) [8]	--	--	1.0×10^{10}	(1.5×10^6)
1-4	[3]	6.4×10^8	(93,500)	--	--	9.9×10^{10}	(14.3×10^6)	--	--
2-1	[4]	--	--	3.3×10^8	(48,000)	--	--	1.7×10^{10}	(2.5×10^6)
2-2	↕	--	--	3.3×10^8	(48,000)	--	--	2.1x	(3.0×10^6)
2-3		--	--	$2.9 \, 10^8$	(42,000)	--	--	2.1x	(3.0×10^6)
2-4	[4]	6.4×10^8	(94,000) [8]	--	--	9.2×10^{10}	(13.8×10^6)	--	--
3-1	[5]			3.9×10^8	(56,000)	--	--	5.9×10^{10}	(2.5×10^6)
3-2	↕			4.3×10^8	(63,000)	--	--	7.1x	(10.3×10^6)
3-3				3.9×10^8	(57,000)	--	--	5.6x	(8.1×10^6)
3-4	[5]	7.8×10^8	(114,000) [8]	--	--	9.5×10^{10}	(13.8×10^6)	--	--
4-1	[6]	--	--	3.4×10^8	(49,000)	--	--	5.3×10^{10}	(7.6×10^6)
4-2	↕	--	--	3.9×10^8	(56,000)	--	--	5.6	(8.1×10^6)
4-3		--	--	3.9×10^8	(56,000)	--	--	6.1	(8.9×10^6)
4-4	[6]	7.4×10^8	(107,000) [8]	--	--	9.5×10^{10}	(13.8×10^6)	--	--
5-1	[7]	--	--	5.0×10^8	(73,000)	--	--	7.2×10^{10}	(10.5×10^6)
5-2	↕	--	--	5.0×10^8	(72,000)	--	--	6.6×10^{10}	(9.5×10^6)
5-3		--	--	4.5×10^8	(65,000)	--	--	6.6×10^{10}	(9.5×10^6)
5-4	[7]	7.2×10^8	(105,000) [8]	--	--	9.1×10^{10}	(13.2×10^6)	--	--

[1] All laminates were initially cured 1 hour at 336°C (636°F) under 1.4×10^6 N/m² (200 psi) pressure.

[2] Head travel was used to determine slope of stress-strain curves to obtain preliminary information on moduli. These values are approximations.

[3] Postcured 3 hours at 371°C (700°F) under 1.4×10^6 N/m² (200 psi) pressure

[4] Postcured 1 hour at 398°C (750°F) under 1.4×10^6 N/m² (200 psi) pressure

[5] Postcured 1.5 hours at 398°C (750°F) under 1.4×10^6 N/m² (200 psi) pressure

[6] Postcured 3 hours at 398°C (750°F) under 1.4×10^6 N/m² (200 psi) pressure

[7] Postcured 1 hour at 427°C (800°F) under 1.4×10^6 N/m2 (200 psi) pressure

[8] These specimens are controls used to verify reproducibility of flexural strength values derived in Task II.

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5.1 (Continued)

Laminates prepared with the 3 candidate postcure schedules were characterized in terms of tensile strength and modulus, shortbeam ILS, and flexure strength and modulus. The results are summarized in Table 17 through Table 19.

From this data, the laminate postcure of 1 hour at 454°C (850°F) under $1.4 \times 10^6 \text{N/m}^2$ (200 psi) pressure was selected as the postcure for BICo (1:3) laminates. This selection was based primarily on laminate flexure strength and modulus at ambient temperature, 202°C (400°F) and 316°C (600°F). The laminates derived from each candidate postcure schedule were examined for their densities and void content, however, the results did not reveal any anomaly to justify a different laminate postcure schedule (See Table 20).

TABLE 17   TENSILE PROPERTIES OF B1 Co(1:3) DERIVED LAMINATES POSTCURED WITH THREE
CANDIDATE POSTCURE SCHEDULES

Item No.	Cure/ Postcure Condition [1]	Strength, N/m^2 (psi)			Modulus N/m^2 (psi)			Comments
		22°C (71°F)	204°C (400°F)	316°C (600°F)	21°C (70°F)	204°C (400°F)	316°C (600°F)	
1	[2]	6.2×10^8 (90,200)	5.7×10^8 (83,200)	5.9×10^8 (85,700)	1.9×10^{11} (27.4×10⁶)	1.6×10^{11} (23.3×10⁶)	1.3×10^{11} (18.8×10⁶)	[5]
2	[3]	5.9×10^8 (86,600)	5.2×10^8 (76,000)	5.8×10^8 (84,100)	1.8×10^{11} (25.4×10⁶)	2.1×10^{11} (28.9×10⁶)	1.3×10^{11} (18.8×10⁶)	[5]
3	[4]	4.7×10^8 (67,800)	5.2×10^8 (75,800)	5.1×10^8 (74,100)	1.6×10^{11} (22.7×10⁶)	2.3×10^{11} (32.8×10⁶)	1.1×10^{11} (15.1×10⁶)	[5]

[1] All laminates were initially cured at 336°C(636°F) under 1.4×10^6 N/m^2 (200 psi) pressure

[2] Postcured 2 hours at 398°C (750°F) under 1.4×10^6 N/m^2 (200 psi)

[3] Postcured 1 hour at 426°C (800°F) under 1.4×10^6 N/m^2 (200 psi)

[4] Postcured 1 hour at 454°C (850°F) under 1.4×10^6 N/m^2 (200 psi)

[5] Average of 3 tests

TABLE 18   SHORT BEAM INTERLAMINAR SHEAR PROPERTIES OF BI Co (1:3) DERIVED LAMINATES POSTCURED WITH THREE CANDIDATE POSTCURE SCHEDULES

Item No.	Cure/ Postcure Conditions	Strength, N/m^2 (psi) △5		
		22°C (71°F)	204°C (400°F)	316°C (600°F)
1	△1 △2	2.8×10^7 (4020)	2.6×10^7 (3800)	2.9×10^7 (4250)
2	△1 △3	3.1×10^7 (4520)	2.8×10^7 (4060)	2.0×10^7 (2720)
3	△1 △4	3.8×10^7 (5550) △6	3.7×10^7 (5,380)	2.5×10^7 (3590)

△1   All laminates were initially cured at 338°C (640°F) under 1.4×10^6 N/m^2 (200 psi)

△2   Postcured 2 hours at 398°C (750°F) under 1.4×10^6 N/m^2 (200 psi)

△3   Postcured 1 hour at 426°C (800°F) under 1.4×10^6 N/m^2 (200 psi)

△4   Postcured 1 hour at 454°C (850°F) under 1.4×10^6 N/m^2 (200 psi)

△5   Average of three tests unless specified

△6   Average of two tests

TABLE 19   FLEXURE PROPERTIES OF BICo (1:3) DERIVED LAMINATES POSTCURED WITH THREE
CANDIDATE POSTCURE SCHEDULES

No.	[1] Cure/ Postcure Condition	Strength, N/m^2 (psi)			Modulus N/m^2 (psi)			Comments
		21°C(7.1°F)	204°C(400°F)	316°C(600°F)	21°C(71°F)	204°C(400°F)	316°C(600°F)	
1	[2]	6.4×10^8(93,000)	5.7×10^8(83,000)	2.5×10^8(36,000)	7.9×10^{10}(11.6x10^6)	8.7×10^{10}(12.6x10^6)	3.1×10^{10}(4.5x10^6)	[5]
2	[3]	5.2×10^8(76,000)	2.6×10^8(38,000)	2.6×10^8(38,000)	6.2×10^{10}(9.0x10^6)	5.5×10^{10}(8.0x10^6)	2.6×10^{10}(3 7x10^7)	[5]
3	[4]	7.2×10^8(105,000)	6.3×10^8(92,000)	4.0×10^8(58,000)	7.9×10^{10}(11.4x10^6)	6.8×10^{10}(9.8x10^6)	4.3×10^{10}(6.2x10^6)	[5]

[1] All laminates were initially cured at 336°C(636°F) under 1.4×10^6 N/m^2 (200 psi)

[2] Postcured 2 hours at 398°C(750°F) under 1.4×10^6 N/m^2 (200 psi)

[3] Postcured 1 hour at 426°C (800°F) under 1.4×10^6 N/m^2 (200 psi)

[4] Postcured 1 hour at 454°C(850°F) under 1.4×10^6 N/m^2 (200 psi)

[5] Average of 3 tests

TABLE 20   DENSITY OF BICo (1:3) DERIVED LAMINATES POSTCURED
WITH 3 CANDIDATE POSTCURE SCHEDULES

Item No.	Postcure Schedule	Density g/ml (21°C)
1	▷1	1.47
2	▷2	1.41
3	▷3	1.39

▷1   Postcured 2 hours @ 398°C (750°F) under 1.4×10^6 N/m^2 (200 psi)

▷2   Postcured 1 hour @ 426°C (800°F) under 1.4×10^6 N/m^2 (200 psi)

▷3   Postcured 1 hour @ 454°C (850°F) under 1.4×10^6 N/m^2 (200 psi)

5.2   Advanced Composite Evaluation

Detailed evaluation tests were conducted using advanced composites fabricated
using the cure and the postcure schedules selected in Tasks II and III respectively.
Table 21 is an outline of the evaluation tests performed under Task III and the test
results are described in paragraphs 5.2.1 through 5.2.8. Emphasis was placed on
determining tensile, flexure, and ILS properties after aging laminates at 204°C
(400°F) and 316°C (600°F). The specimens subjected to 1000 hours aging at
316°C were not tested because of loss of matrix polymer due to the exposure
environment. Considerable matrix material depolymerized and volatilized,
leaving large portions of exposed graphite fibers. Although the test specimens
were not weighed before aging, it is estimated that 50% to 80% of the original
matrix polymer was volatilized. This polymer loss roughly corresponds to laminate
weight losses of 25% to 40%. Lower laminate weight losses were obtained during the
formal isothermal aging program (see paragraph 5.2.8) where a laminate weight
loss of 16% was obtained after aging 1000 hours at 316°C (600°F). Films of pure
block copolymer, in contrast, displayed a very small weight loss of 1.24% after
aging 1100 hours at 316°C (600°F), (see Table 3, paragraph 3.2) which is in direct
conflict with the composite data. In the absence of additional data, a firm
hypothesis of what causes the observed loss of matrix during 316°C (600°F) aging
of BICo (1:3)/graphite laminates, cannot be made. As speculation, the loss of
BICo (1:3) polymer during aging of laminates at 316°C (600°F) may be attributed
to interplays of several factors, for example, the high postcure temperature; carbon
fibers catalyzing the decomposition of the polymer; or catalytic interactions of
solvent-modified graphite surfaces with the polymer at the elevated temperatures.

5.2.1   Effect of Aging at 204° C (400°F) and 316°C (600°F) on
                  Tensile Strength and Modulus of Advanced Composites

Tensile strength and moduli of BICo (1:3) graphite composites were determined as
outlined in Table 21. Table 22 summarizes the tensile strength results and Table 23
summarizes the moduli of BICo (1:3) advanced composites. Figures 18 and 19 show
tensile and moduli changes due to aging laminates at 204°C and at 316°C.

The 90° unidirectional tests were conducted to determine the transverse tensile
porperties of the composites, or in essence measuring the strength of the matrix.

TABLE 21   SUMMARY OF ADVANCED COMPOSITE TESTS

Property	Test Temp. °C (°F)	Exposure Temp., °C (°F)	Exposure Time In Air, Hrs.	No. Unid.	Specimens 0°/90°
Tensile Strength and Modulus	Ambient 204(400) ↓	-- 204(400) ↓	-- 0.1 100 500 1000	10 ↓ ⟦1⟧	3 ↓
	316(600) ↓	316(600) ↓	0.1 100 500 1000	10 ↓	3 ↓
Flexural Strength and Modulus	Ambient 204(400) ↓	-- 204(400) ↓	-- 0.1 100 500 1000	10 ↓	3 ↓
	316(600) ↓	316(600) ↓	0.1 100 500 1000	10 ↓	3 ↓
Interlaminar Shear	Ambient 204(400) ↓	-- 204(400) ↓	-- 0.1 100 500 1000	10 ↓	- ↓
Thermal Cycling	Ambient	--	--	5	5
Creep	Ambient 260(500)	-- --	200 200	3 3	3 3
Thermal Expansion Longitudinal Transverse Thickness	⟦2⟧ ⟦2⟧ ⟦2⟧	-- -- --	-- --- --	2 2 2	2 1 1
Hydrolytic Stability	Ambient	--	3.0	5	-

⟦1⟧   Five (5) specimens for transverse properties and five (5) specimens for longitudinal tensile strength and modulus at ambient temperature

⟦2⟧   -195 to 316°C (-320° to 600°F)

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Table 22. TENSILE STRENGTH OF BLOCK COPOLYMER (1:3)/GRAPHITE COMPOSITES EXPOSED AND TESTED AT 204°C (400°F) AND 316°C (600°F)

Test Temp °C (°F)	Exposure Temp °C (°F)	Exposure Time (hrs)	0° Longitudinal Strength, N/m² (psi)			0°/90° Strength, N/m² (psi) [4]			COMMENTS
			High	Low	Average	High	Low	Average	
Ambient	-	-	8.7×10^8 (126,800)	5.3×10^8 (76,700)	7.0×10^8 (101,500)	6.1×10^8 (88,200)	4.3×10^8 (63,000)	5.2×10^8 (75,900)	[1] [2]
204 (400)	204 (400)	.1	7.0×10^8 (101,000)	5.2×10^8 (75,000)	5.7×10^8 (83,100)	4.7×10^8 (68,600)	3.9×10^8 (56,600)	4.4×10^8 (64,200)	[2] [3]
		100	9.4x (136,000)	5.6x (81,600)	6.9x (100,300)	5.2x (75,800)	5.1x (73,500)	5.2x (75,000)	[2] [3]
		500	8.7x (126,800)	5.5x (80,000)	6.5x (94,700)	4.8x (70,000)	3.3x (48,500)	3.9x (57,100)	[2] [3]
		1000 [5]	8.9x (129,500)	4.4x (63,100)	7.1x (103,600)	3.9x (57,100)	3.3x (47,400)	3.5x (51,100)	[2] [3]
316 (600)	316 (600)	.1	9.5×10^8 (137,600)	3.8×10^8 (54,900)	7.0×10^8 (101,400)	5.1×10^8 (74,200)	3.2×10^8 (46,200)	4.2×10^8 (61,400)	[2] [3]
		100	9.7x (141,000)	6.2x (90,100)	7.4x (107,900)	4.5x (65,000)	3.7x (53,200)	4.0x (57,800)	[1] [3]
		500	6.5x (94,700)	3.0x (43,800)	4.9x (70,600)	2.2x (31,600)	1.3x (18,500)	1.8x (25,400)	[2] [2]
		1000 [5]							
			0° Transverse Strength						
Ambient	-	-	1.2×10^7 (1,700)	3.1×10^6 (450)	7.6×10^6 (1,100)				[1]

[1] All 0° and 90° unidirectional results at ambient temperatures are based on 5 tests

[2] All 0°/90° test results are based on 3 tests at each test temperature

[3] All 0° unidirectional results at elevated temperatures are based on 10 tests at each test temperature

[4] Ratio of 0°/90° = 2/1

[5] Specimens aged 1000 hrs at 316°C were not tested for tensile properties because of excessive loss of matrix material from the laminate

Table 23. TENSILE MODULUS OF BLOCK COPOLYMER (1:3)/GRAPHITE COMPOSITES EXPOSED AND TESTED AT 204°C (400°F) AND 316°C (600°F)

Test Temp °C (°F)	Exposure Temp °C (°F)	Exposure Time (hrs)	0° Longitudinal Modulus, N/m² (psi) High	Low	Average	0°/90° Modulus, N/m² (psi) High	Low	Average	Comments
Ambient	-	-	2.1×10^{11} (30.0×10^6)	1.1×10^{11} (16.4×10^6)	1.7×10^{11} (24.4×10^6)	2.5×10^{11} (36.8×10^6)	1.1×10^{11} (16.1×10^6)	1.7×10^{11} (24.8×10^6)	[1] [2]
204 (400)	204 (400)	.1	7.9×10^{10} (11.5×10^6)	5.8×10^{10} (8.4×10^6)	7.0×10^{10} (10.1×10^6)	2.2×10^{11} (32.5×10^6)	7.9×10^{10} (11.5×10^6)	1.4×10^{11} (19.6×10^6)	[1]
		100	2.0×10^{11} ($29.0x$)	$9.9x$ ($14.3x$)	1.4×10^{11} ($20.6x$)	9.4×10^{10} ($13.6x$)	$8.9x$ ($12.9x$)	9.1×10^{10} ($13.3x$)	
		500	$1.4x$ ($20.6x$)	$9.9x$ ($14.3x$)	$1.2x$ ($17.1x$)	$8.9x$ ($12.9x$)	$7.0x$ ($10.1x$)	$7.7x$ ($11.2x$)	
		1000	$1.5x$ ($22.0x$)	$8.9x$ ($12.9x$)	$1.3x$ ($18.5x$)	$8.4x$ ($12.2x$)	$6.8x$ ($9.8x$)	$7.4x$ ($10.8x$)	
316 (600)	316 (600)	.1	1.4×10^{11} (20.3×10^6)	5.6×10^{10} (8.1×10^6)	1.3×10^{11} (19.3×10^6)	8.9×10^{10} (12.9×10^6)	8.2×10^{10} (11.9×10^6)	8.7×10^{10} (12.0×10^6)	
		100	$1.7x$ ($25.2x$)	$8.2x$ ($11.9x$)	$1.3x$ ($19.3x$)	$1.0x$ ($15.0x$)	$8.5x$ ($12.3x$)	$9.2x$ ($13.3x$)	
		500	$1.4x$ ($19.9x$)	$5.8x$ ($8.4x$)	$1.1x$ ($15.7x$)	$5.8x$ ($8.4x$)	$4.3x$ ($6.3x$)	$4.8x$ ($7.0x$)	
		1000 [5]	-	-	-	-	-	-	[3]

0° Transverse Modulus

			0° Longitudinal Modulus, N/m² (psi) High	Low	Average
Ambient	-	-	1.4×10^{10} (2.0×10^6)	0.9×10^{10} (1.3×10^6)	1.2×10^{10} (1.8×10^6)

[1] All 0° and 90° unidirectional results at ambient temperatures are based on 5 tests

[2] All 0°/90° test results are based on 3 tests at each test temperature

[3] All 0° unidirectional results at elevated temperatures are based on 10 tests at each test temperature

[4] Ratio of 0°/90° = 2/1

[5] Specimens aged 1000 hrs at 316°C were not tested for tensile properties because of excessive loss of matrix material from the laminate.

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Figure 18 : TENSILE STRENGTH OF UNIDIRECTIONAL BICo (1:3) LAMINATES EXPOSED
AND TESTED AT 204°C (400°F) AND 316°C (600°F)

△ TESTED AT 204°C (400°F)

○ TESTED AT 316°C (600°F)

204°C (400°F)

316°C (600°F)

TESTED AT ROOM
TEMPERATURE

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Figure 19: TENSILE MODULUS OF UNIDIRECTIONAL BICo (1:3) LAMINATES EXPOSED AND TESTED AT 204°C (400°F) AND 316°C (600°F)

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5.2.2   Effect of Aging at 204°C (400°F) and 316°C (600°F) on Flexural Strength and Modulus of Advanced Composites

Flexure strength and modulus of BICo (1:3) advanced composites were determined as outlined in Table 21. Table 24 summarizes the flexure strength and Table 25 summarizes the modulus of BICo(1:3) graphite composites. The effect of exposure at 204°C and 316°C on flexure strength and modulus are also summarized in Figures 20 and 21. Flexure strength and modulus were determined from the same specimen.

5.2.3   Effect of Aging at 204°C (400°F) and 316°C (600°F) on Interlaminar Shear (Short Beam) of Advanced Composites

Short beam interlaminar shear (ILS) strength of BICo (1:3) advanced composites were determined as outlined in Table 21. Table 26 summarizes the ILS test results.

5.2.4   Effect of Thermal Cycling, -54°C (-65°F) to 316°C (600°F), on Tensile Properties of Advanced Composites

BICo(1:3) laminates were thermally cycled one hundred times between -51°C and 316°C and tested for tensile strength at room temperature. The test results are summarized in Table 27. After thermal cycling, the test specimens were examined visually. Damage (such as crazing and cracking) caused by the exposure was not observed.

5.2.5   200 Hour Creep Tests at Ambient Temperature and 260°C (500°F)

Creep tests on tensile specimen were conducted in accordance with Table 21. Initially, specimens were loaded to 80% of the average of their ultimate stress at room temperature (refer to Table 22). This load led to failure, in tensions during loading the first three specimens. Since the static load level initially selected was based on an average of ultimate stresses, the observed failures may be attributed to statistics. The creep test stress was lowered to 50% of ultimate stress and the remaining specimen tested for 200 hours creep. Creep was not observed under these conditions. Table 28 summarizes the test parameters used.

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TABLE 24 FLEXURE STRENGTH OF BLOCK COPOLYMER (1:3)/GRAPHITE COMPOSITES
EXPOSED AND TESTED AT 204°C (400°F) AND 316°C (600°F)

Test Temp °C (°F)	Exposure Temp °C (°F)	Exposure Time (hrs)	0° Unidirectional Strength, N/m² (psi)			0°/90° Strength, N/m² (psi)		
			High	Low	Average [1]	High	Low	Average [2] [3]
Ambient	-	-	1.1×10^9 (154,600)	4.1×10^8 (59,600)	8.3×10^8 (120,800)	4.4×10^8 (64,300)	3.1×10^8 (45,100)	3.6×10^8 (52,000)
204 (400)	204 (400)	.1	8.9×10^8 (128,600)	6.4×10^8 (92,200)	7.8×10^8 (113,600)	4.9×10^8 (70,600)	2.6×10^8 (37,000)	3.7×10^8 (54,300)
		100	9.0x (130,400)	5.8x (84,000)	8.1x (117,700)	4.6x (66,700)	3.0x (43,000)	3.6x (52,500)
		500	8.0x (115,800)	5.2x (75,100)	6.7x (98,000)	4.7x (68,300)	3.3x (48,200)	4.0x (58,300)
		1000	7.4x (108,000)	5.2x (75,700)	6.1x (88,900)	3.8x (55,600)	3.2x (46,200)	3.6x (52,400)
316 (600)	316 (600)	.1	7.8×10^8 (113,400)	3.7×10^8 (53,400)	6.0×10^8 (87,200)	4.6×10^8 (66,300)	3.1×10^8 (44,400)	3.6×10^8 (51,700)
		100	7.6x (110,500)	4.5x (64,700)	6.7x (96,800)	4.2x (60,800)	2.0x (28,400)	3.0x (43,900)
		500	7.2x (104,800)	1.7x (24,500)	3.6x (51,900)	7.7×10^7 (11,200)	2.3×10^7 (3,400)	4.8×10^7 (7,050)
		1000 [4]	---					---

[1] All 0° unidirectional test results are based on 10 tests at each test temperature

[2] All 0°/90° test results are based on 3 tests at each test temperature

[3] Ratio of 0°/90° = 2/1

[4] Specimens aged 1000 hrs. at 316°C were not tested for flexure properties because of excessive loss of matrix material from the laminate
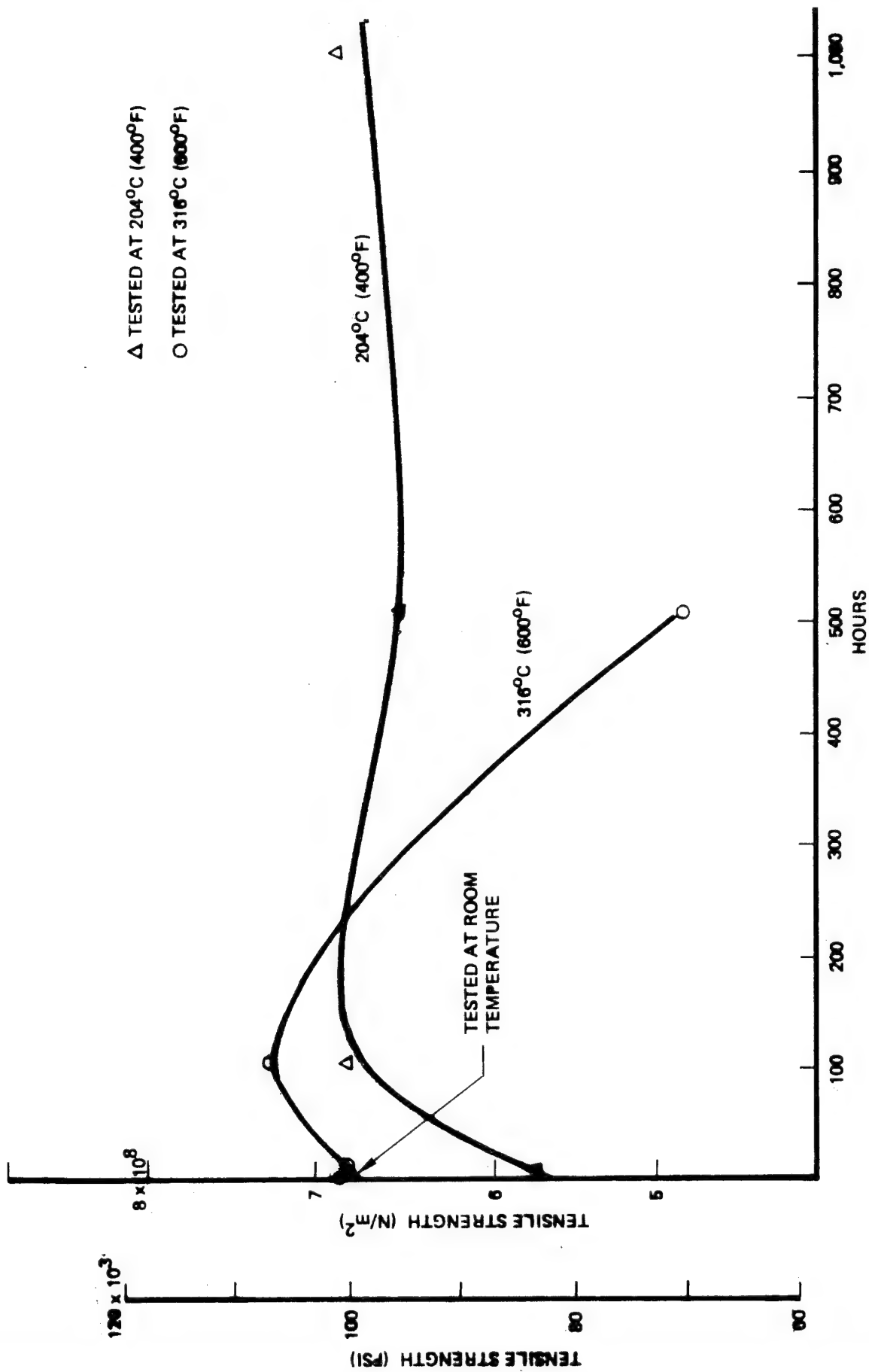
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TABLE 25 FLEXURE MODULUS OF BLOCK COPOLYMER (1:3)/GRAPHITE COMPOSITES EXPOSED AND TESTED AT 204°C (400°F) AND 316°C (600°F)

Test Temp °C	Test Temp °C	Exposure Time (hrs)	0° Unidirectional Modulus, N/m² (psi)			0°/90° Modulus, N/m² (psi) [3]			Comments
			High	Low	Average [1]	High	Low	Average [2]	
Ambient	-	-	2.4×10^{11} (35.2×10^6)	9.9×10^{10} (14.4×10^6)	1.35×10^{11} (19.6×10^6)	7.9×10^{10} (11.5×10^6)	5.6×10^{10} (8.3×10^6)	6.6×10^{10} (9.5×10^6)	
204	204	.1	1.2×10^{11} (17.2×10^6)	7.1×10^{10} (10.3×10^6)	9.5×10^{11} (13.8×10^6)	8.3×10^{10} (12.3×10^6)	5.2×10^{10} (7.5×10^6)	7.2×10^{10} (10.4×10^6)	
		100	1.3x (18.9x)	9.3x (13.5x)	1.1x (16.1x)	8.2x (11.9x)	4.6x (6.6x)	9.8x (8.7x)	
		500	1.2x (18.0x)	7.2x (10.5x)	1.0x (15.1x)	8.6x (12.4x)	6.3x (9.2x)	7.5x (10.8x)	
		1000	1.0x (14.7x -)	6.4x (9.3x)	8.1x (11.7x)	5.9x (9.6x)	5.5x (7.9x)	6.2x (9.0x)	
316	316	.1	1.3×10^{11} (18.2×10^6)	5.0×10^{10} (7.2×10^6)	8.3×10^{11} (12.5×10^6)	9.2×10 (13.3×10^6)	4.5×10^{10} (6.5×10^6)	4.5×10^{10} (6.5×10^6)	
		100	2.2x (31.6x)	9.4x (13.6)	1.2x (16.8x)	1.4x (21.0x)	3.6x (5.3x)	3.6x (5.3x)	
		500	2.3x (33.5x)	4.5x (6.5x)	1.0x (15.4x)	7.6×10^9 (1.1x)	4.1×10^9 (.6x)	6.9×10^9 (1.0x)	[4]
		1000	—	—	—	—	—	—	

[1] All 0° unidirectional test results are based on 10 tests at each test temperature

[2] All 0°/90° test results are based on 3 tests at each test temperature

[3] Ratio of 0°/90° = 2/1

[4] Specimens aged 1000 hrs at 316°C were not tested for flexure properties because of excessive loss of matrix material from the laminates

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Figure 20 : FLEXURE STRENGTH OF UNIDIRECTIONAL BI Co (1:3) LAMINATES EXPOSED AND TESTED AT 204°C (400°F) AND 316°C (600°F)
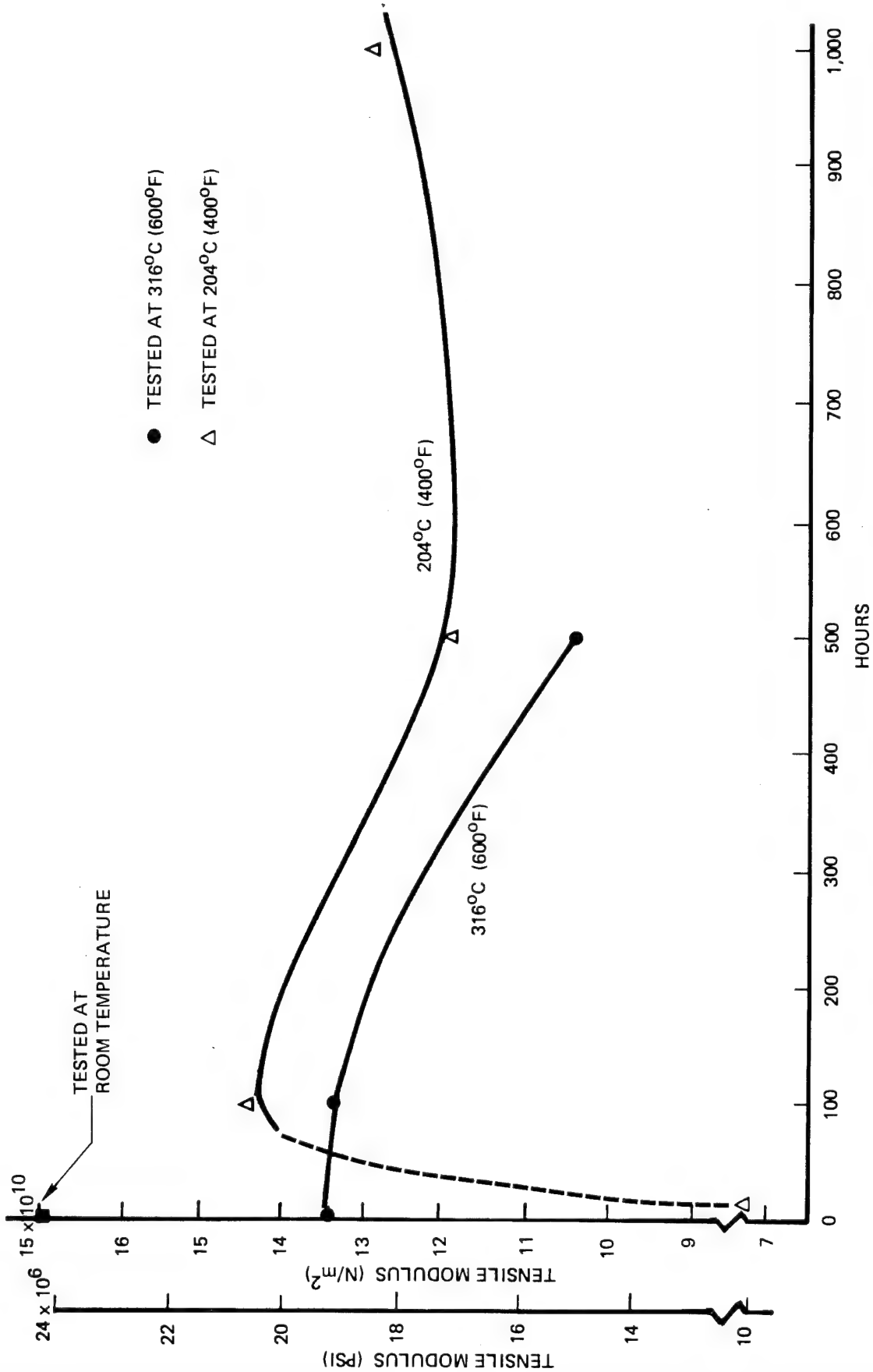
74
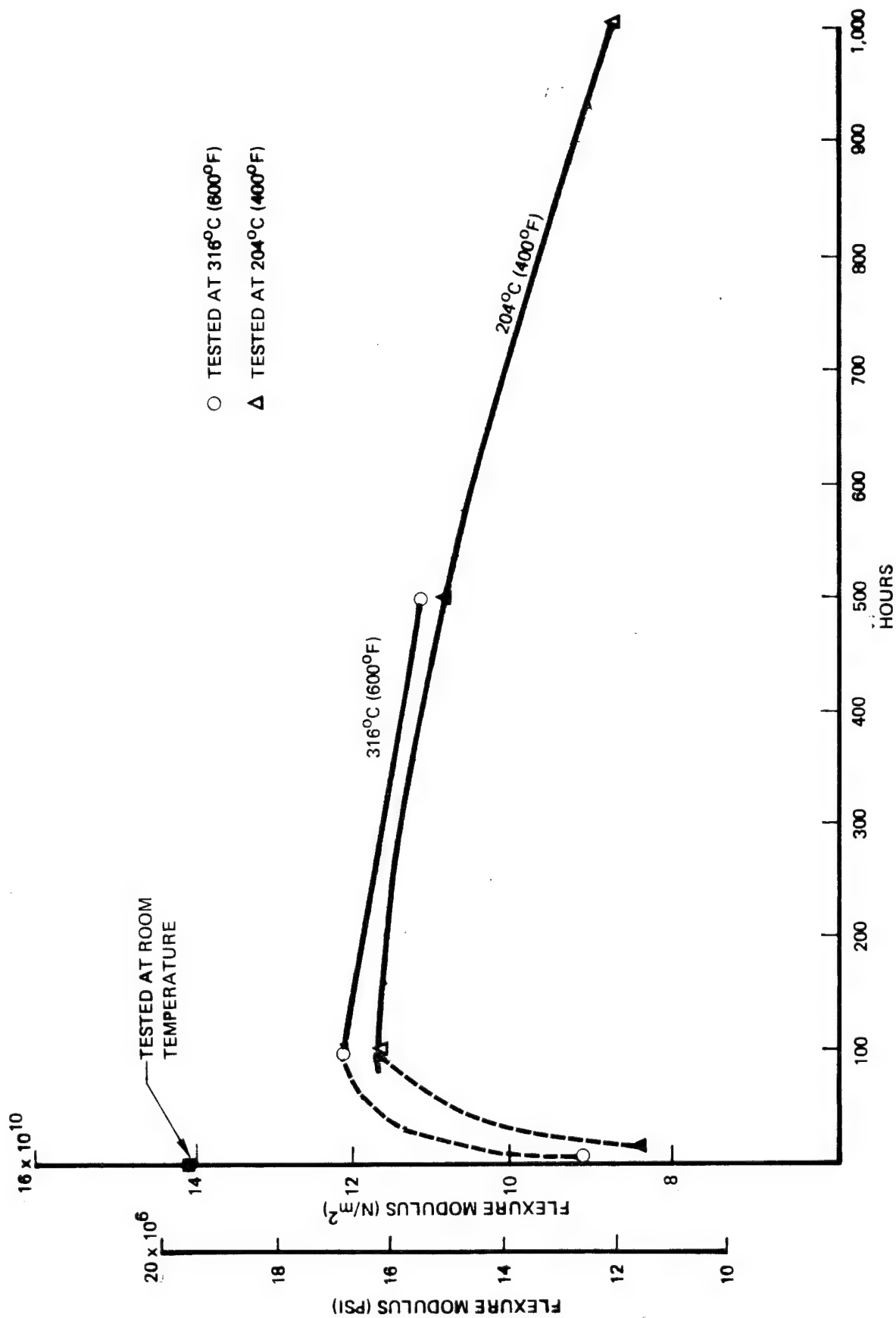
Figure 21 : FLEXURE MODULUS OF UNIDIRECTIONAL BI Co (1:3) LAMINATES EXPOSED AND TESTED AT 204°C (400°F) AND 316°C (600°F)

Table 26   INTERLAMINAR SHEAR STRENGTH (SHORT BEAM) OF BLOCK
COPOLYMER (1:3)/GRAPHITE COMPOSITES EXPOSED AND
TESTED AT 204°C (400°F) AND 316°C (600°F)

Test Temp. °C (°F)	Exposure Temp. °C (°F)	Exposure Time (Hrs)	Strength, N/m² (psi)		Average [1]
			High	Low	
Ambient	-	-	4.0×10^7 (5860)	1.5×10^7 (2130)	2.9×10^7 (4220)
204 (400)		.1	4.1×10^7 (5970)	1.5×10^7 (2220)	3.0×10^7 (4250)
	204 (400)	100	4.0X (5850)	2.5X (3590)	3.6X (5150)
		500	4.1X (5940)	2.7X (3890)	3.4X (4960)
		1000	3.4X (4960)	2.3X (3270)	2.8X (4060)
316 (600)		.1	2.9×10^7 (4260)	1.7×10^7 (2420)	2.1×10^7 (3110)
	316 (600)	100	3.6X (5220)	2.7X (3930)	3.1X (4550)
		500	2.8X (4140)	9.2×10^6 (1330)	1.9X (2780)

⚠ 1   Test results are based on 10 tests at each test temperature.

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Table 27. TENSILE STRENGTH AND MODULUS OF THERMALLY CYCLED LAMINATES
[-54°C (-65°F) to 316°C (600°F)]

Item No.	Strength, N/m² (psi) [1]			Modulus, N/m² (psi) [1]			Laminate Type
	High	Low	Average	High	Low	Average	
Control	8.7×10^8 (126,800)	5.3×10^8 (76,700)	7.0×10^8 (101,500)	2.1×10^{11} (30x10^6)	1.1×10^{11} (16.4x10^6)	1.7×10^{11} (24.8x10^6)	0°
1	7.7×10^8 (112,000)	4.4×10^8 (64,000)	6.4×10^8 (92,700)	1.5×10^{11} (21.8x10^6)	5.4×10^{10} (7.8x10^6)	9.4×10^{10} (13.6x10^6)	0°
Control	6.1×10^8 (88,200)	4.3×10^8 (63,000)	5.2×10^8 (75,900)	2.5×10^{11} (36.8x10^6)	1.1×10^{11} (16.1x10^6)	1.7×10^{11} (24.8x10^6)	0°/90°
2	5.2×10^8 (76,000)	3.6×10^8 (52,400)	4.8×10^8 (69,100)	8.0×10^{10} (11.6x10^6)	4.9×10^{10} (7.1x10^6)	6.2×10^{10} (9.0x10^6)	0°/90°

[1] All tests were conducted at ambient temperature. Test results are based on an average of 5 tests for each type of laminate.

Table 28 . TEST PARAMETERS USED IN ROOM TEMPERATURE AND 260°C (500°F) 200-HOUR CREEP TESTS.

Item No.	Fiber Direction	Test Temp °C	Test Stress N/m² (psi)	Loading Time Hrs	Loading Strain cm/cm (in/in)	Creep Strain	Comments
1	0°	22	5.6×10^8 (81,200)	.03	—	—	△1
2	0°	22	5.6×10^8		—	—	△1
3	0°	22	5.6×10^8 (81,200)		—	—	△1
3-1	0°	22	3.5×10^8 (50,700)	.03	—	—	△2
4	0°/90°	22	2.6×10^8 (37,900)	.03	.0066 (.00258)	0	
5	0°/90°	22	2.6×10^8		.0051 (.00202)	0	
6	0°/90°	22	2.6×10^8 (37,900)	.03	.0044 (.00175)	0	
7	0°	260	2.8×10^8 (40,400)	.03	.0056 (.00220)	0	
8	0°	260	2.8×10^8		.0030 (.00120)	0	
9	0°	260	2.8×10^8 (40,400)	.03	.0038 (.00153)	0	
10	0°/90°	260	3.4×10^8 (34,100)	.03	.0065 (.00255)	—	△1
11	0°/90°	260	3.4×10^8		.0045 (.00177)	0	
12	0°/90°	260	3.4×10^8 (34,100)	.03	.0049 (.00195)	—	△2

△1 Failed on loading.

△2 Failed in grip.

5.2.6　　　　　　　　　Thermal Expansion Between −196°C(−320°F) and 316°C (600°F)
　　　　　　　　　　　 of BlCa (1:3) Composites

Coefficients of thermal expansion of advanced composites were determined in accordance with Table 21. The test results are summarized in Table 29.

5.2.7　　　　　　　　　Hydrolytic Stability of Advanced Composites

Short beam ILS specimens were kept under boiling water for two hours, and their strength determined at ambient temperature. The test results are summarized below:

Specimen	Strength, N/m^2 (psi)	
1	3.9×10^7	(5610)
2	3.5×10^7	(5090)
3	3.9×10^7	(5640)
4	4.1×10^7	(5930)
5	4.5×10^7	(6520)
	4.0×10^7	(5760)

Prior to ILS tests, the specimens were dried and weighed. Weight gains of less than 1% were obtained. The ILS strength values of water boiled ILS specimens compare favorably with values obtained from specimens not subjected to this hydrolytic stability test. As shown in Table 26, the room temperature ILS strength of regular ILS tests is 2.9×10^7 N/m^2 (4220 psi). This is an average value of ten tests.

5.2.8　　　　　　　　　Isothermal Aging (204°C(400°F)) and 316°C(600°F) of
　　　　　　　　　　　 Advanced Composites

Laminates of 1.9 x .64 x .25 cm in size were aged 1000 hours of 204°C and at 316°C. The weight loss results are summarized in Figure 22.

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TABLE 29 COEFFICIENT OF THERMAL EXPANSION OF ADVANCED COMPOSITES

Axis	Run No.	0° UNIDIRECTIONAL, mm/mm/°C (in/in/°F)			Run No.	0°/90° BIDIRECTIONAL, mm/mm/°C (in/in/°F)		
		−196° to 24°C [1]	24° to 191°C [2]	24° to 316°C [3] [4]		−196° to 24°C [1]	24° to 191°C [2]	24° to 316°C [3] [4]
Longitudinal	1	2.7×10^{-5} ($.6 \times 10^{-6}$)	3.15×10^{-5} ($.69 \times 10^{-6}$)	2.0×10^{-5} ($.45 \times 10^{-6}$)	1	0	-1.6×10^{-5} ($-.36 \times 10^{-6}$)	-2.7×10^{-5} ($-.6 \times 10^{-6}$)
	2	2.7×10^{-5} ($.6 \times 10^{-6}$)	2.92×10^{-5} ($.64 \times 10^{-6}$)	2.0×10^{-5} ($.45 \times 10^{-6}$)	2'	0	-1.2×10^{-5} ($-.26 \times 10^{-6}$)	-2.3×10^{-5} ($-.5 \times 10^{-6}$)
Transverse	1	7.7×10^{-4} (16.8×10^{-6})	9.7×10^{-4} (21.2×10^{-6})	9.3×10^{-4} (20.5×10^{-6})	1	1.2×10^{-5} (2.7×10^{-6})	5.5×10^{-5} (1.2×10^{-6})	5.2×10^{-5} (1.14×10^{-6})
	2	7.0×10^{-4} (15.4×10^{-6})	7.9×10^{-4} (17.3×10^{-6})	4.8×10^{-4} (10.5×10^{-6})	2	7.8×10^{-4} (1.7×10^{-6})	2.0×10^{-4} (4.5×10^{-6})	1.1×10^{-5} (2.5×10^{-6})
Thickness	1	1.2×10^{-3} (27.2×10^{-6})	8.9×10^{-4} (19.6×10^{-6})	1.1×10^{-3} (24.1×10^{-6})	1	2.2×10^{-4} (4.9×10^{-6})	3.4×10^{-4} (7.5×10^{-6})	3.0×10^{-4} (6.5×10^{-6})
	2	1.3×10^{-3} (27.6×10^{-6})	1.4×10^{-3} (31.3×10^{-6})	1.5×10^{-3} (32.6×10^{-6})				

[1] −320°F to 75°F

[2] 75°F to 375°F

[3] 75°F to 600°F

[4] 50% by Volume Resin Content

[5] 191° to 316°C (350°F to 600°F) the Thermal Expansion was 8.6×10^{-5} mm/mm/°C (1.9×10^{-6} in/in/°F)
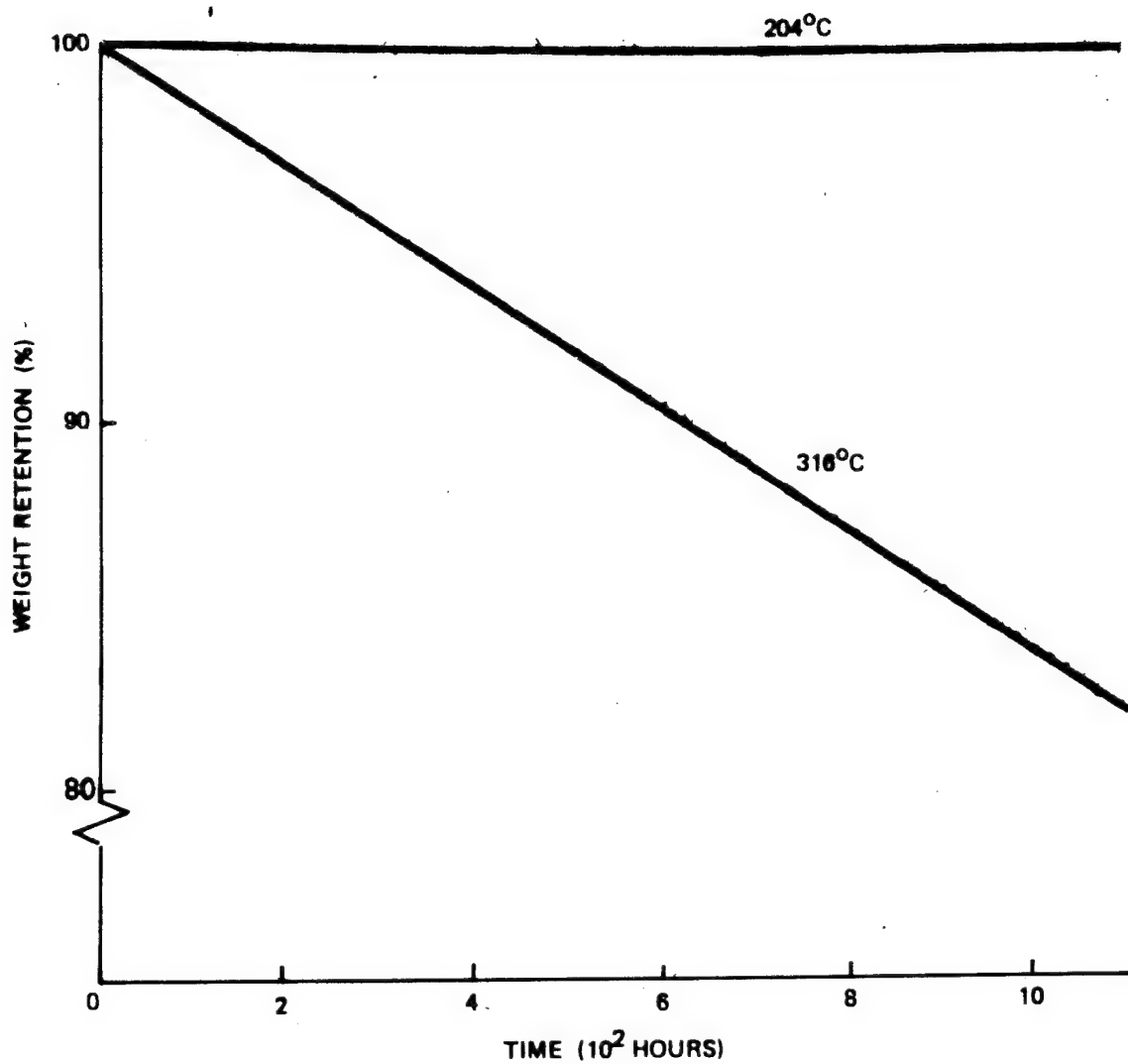
Figure 22 *ISOTHERMAL AGING OF BiCo (1:3) LAMINATES AT 204°C (400°F) AND 316°C (600°F)*

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6.0 CONCLUSIONS AND RECOMMENDATIONS

1. PPQ graphite fiber laminates can be processed at relatively low pressures. Laminating pressures were held below 1.4×10^6 N/m^2 (200 psi), however, post-cure temperatures of 459°C (850°F) maximum were required. The resulting composites contained less than 2% voids. It may be possible to lower the cure and postcure temperature by synthetic modification on the PPQ which may improve the processability while retaining high temperature performance.

2. Room temperature tensile, flexural and interlaminar shear strength properties of PPQ/HMS graphite composites have proven equivalent to epoxy/HMS graphite composite systems. Block copolymer (1:3) graphite composites have exhibited some potential for short term service at 371°C (700°F) and continuous use at 316°C (600°F). After aging 500 hours at 316°C (600°F) in air laminates made with this polymer had a flexural modulus of 1.0×10^{11} N/m^2 (15.4×10^6 psi) at 316°C (600°F) and a flexural strength of 3.6×10^8 N/m^2 (51,900 psi).

3. The PPQ polymers in both powder and film form exhibited better thermal oxidative stability than did the graphite fiber laminates which used the same polymers. Analysis of the results suggest the following: (1) the high postcure temperature initiates polymer degradation by an undefined mechanism; (2) there is a detrimental interaction between the polymer and the graphite with the latter possibly acting as catalyst for initiating degradation; (3) an interaction of solvent-modified graphite surface with the polymer causes the degradation at elevated temperature. Additional investigation into this phenomenon is recommended since it may have direct bearing on the elevated temperature performance of the PPQ and other high temperature polymers with graphite fiber reinforcements.

4. BICo (1:3) laminates demonstrated excellent hydrolytic stability. After standing in boiling water for two hours ILS test specimens had an average room temperature strength of 4.0×10^7 N/m^2 (5760psi) compared to controls which had an average ILS of 2.9×10^7 N/m^2 (4220 psi).

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6.0   (Continued)

5.   The resistance of Bl Co (1:3) laminates to creep at room temperature and at
     260°C (500°F) was demonstrated. A static load of 50% ultimate stress for
     Bl Co (1:3) laminates did not produce measurable creep at the test temperatures.

6.   Bl Co (1:3) laminate demonstrated good resistance to thermal cycling between
     -54°C (-65°F) and 316°C (600°F). Laminate damage, such as crazing and
     cracking, was not observed after exposure of tensile specimens through 100
     cycles between -54°C (-65°F) and 316°C (600°F). After thermal cycling
     the exposed specimens exhibited, relative to controls, a small decrease of
     9% in room temperature tensile strength.

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21.   Air Force Structural Design Guide for Advanced Composites Application

APPENDIX

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Figure A-1: SCANNING ELECTRON PHOTOMICROGRAPHS OF SINGLE GRAPHITE
FIBERS IMPREGNATED IN PPQI (POLYMER 2, TABLE 2) X1400

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Figure A-2: SCANNING ELECTRON PHOTOMICROGRAPHS OF "SINGLE" GRAPHITE
FIBERS IMPREGNATED IN PPQI (POLYMER 3, TABLE 2) X1400

Figure A-3: SCANNING ELECTRON PHOTOMICROGRAPHS OF "SINGLE" GRAPHITE
FIBERS IMPREGNATED IN PPQ II (POLYMER 5, TABLE 2) X1400
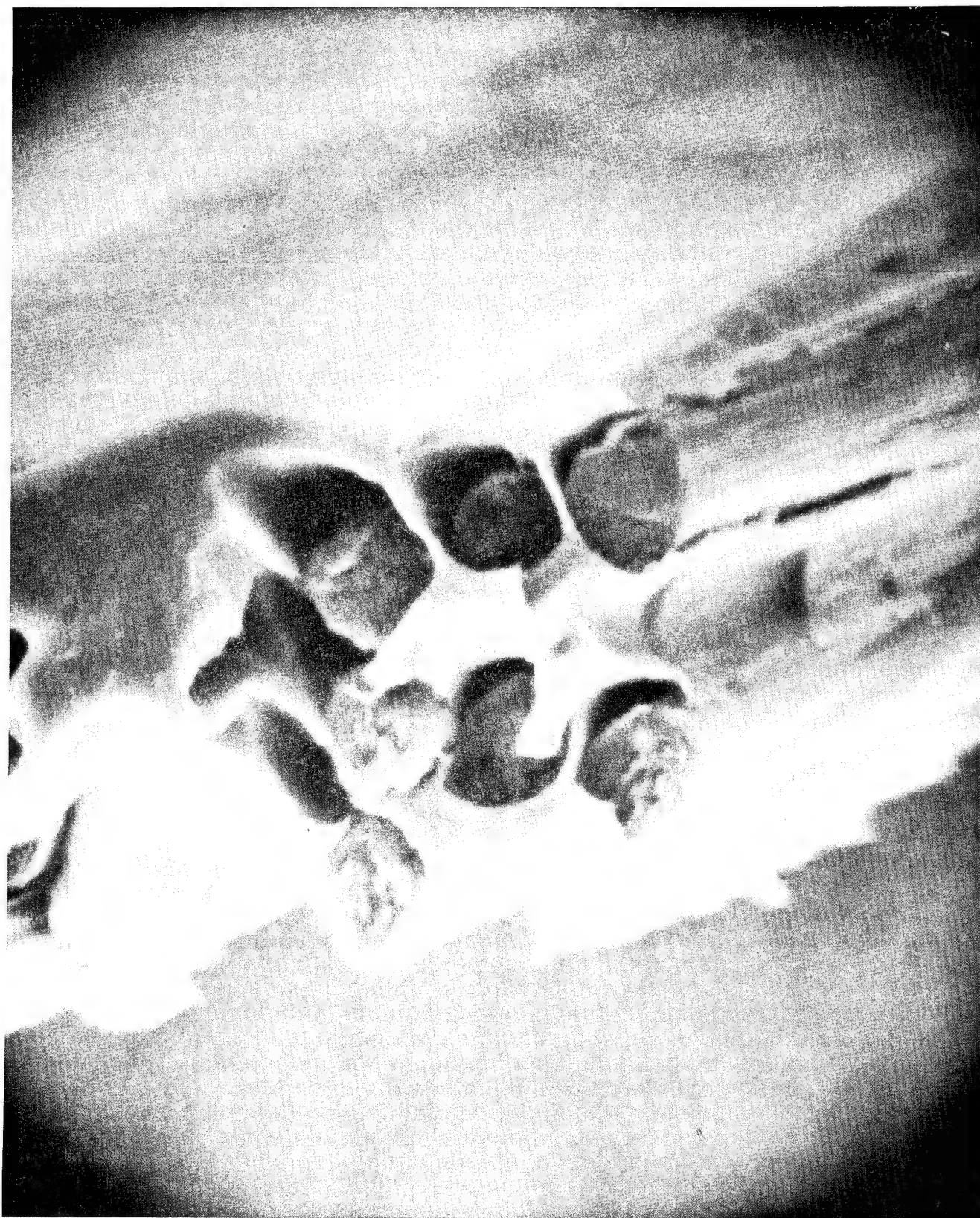
Figure A-4: SCANNING ELECTRON PHOTOMICROGRAPHS OF "SINGLE" GRAPHITE
FIBERS IMPREGNATED IN 1:3 RANDOM COPOLYMER (POLYMER 9, TABLE 2) X1400

92
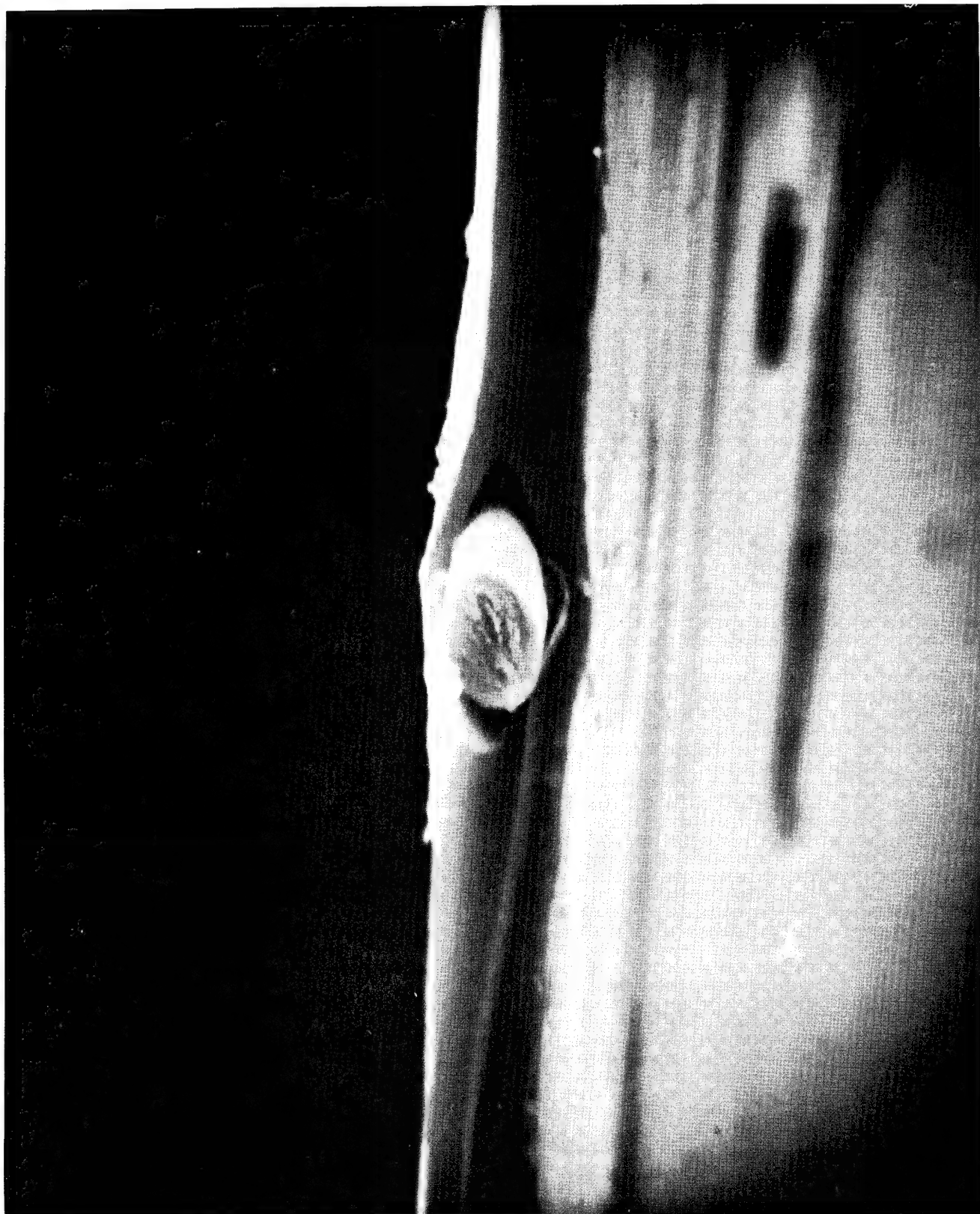
Figure A-5: *SCANNING ELECTRON PHOTOMOCROGRAPHS OF "SINGLE" GRAPHITE FIBERS IMPREGNATED IN 1:3 BLOCK COPOLYMER (POLYMER 12, TABLE 2) X1400*

93
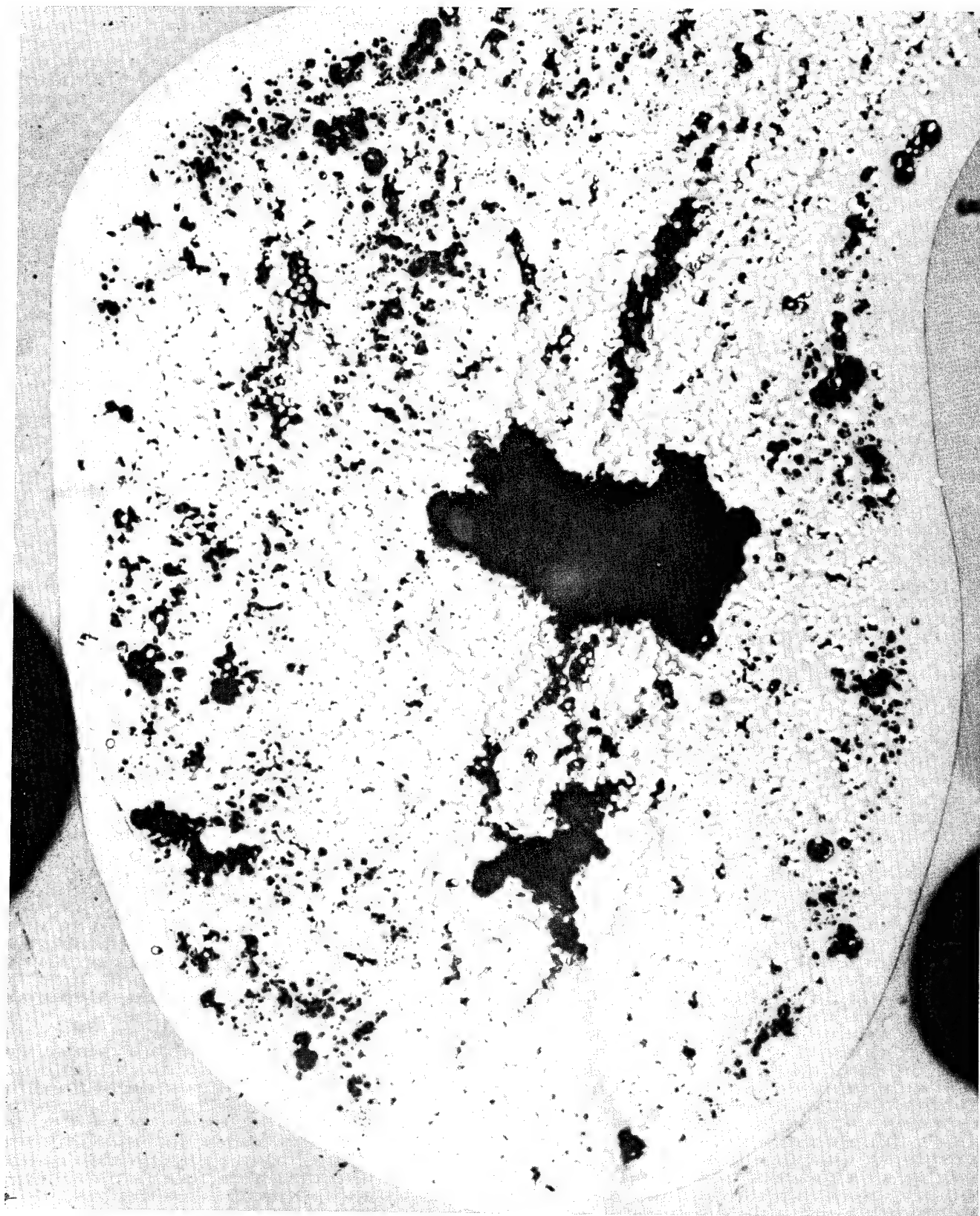
Figure A-6: CROSS SECTION OF DRIED GRAPHITE TOW IMPREGNATED WITH PPQI (POLYMER 2, TABLE 2) X80

Figure A-7:   CROSS SECTION OF DRIED GRAPHITE TOW IMPREGNATED WITH PPQI
(POLYMER 3, TABLE 2) X80
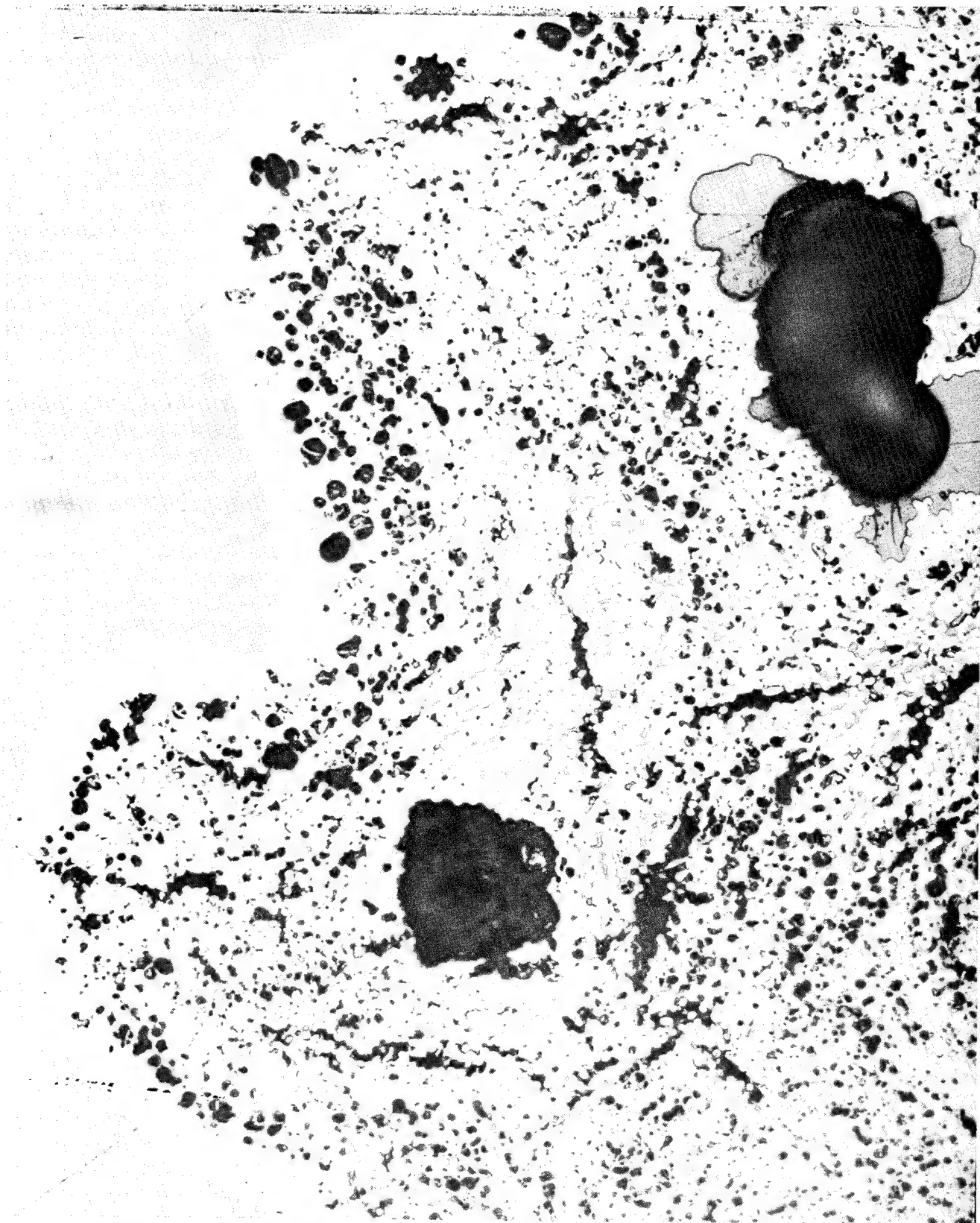
Figure A-8: CROSS SECTION OF DRIED GRAPHITE TOW IMPREGNATED WITH PPQII
(POLYMER 5, TABLE 2) X80
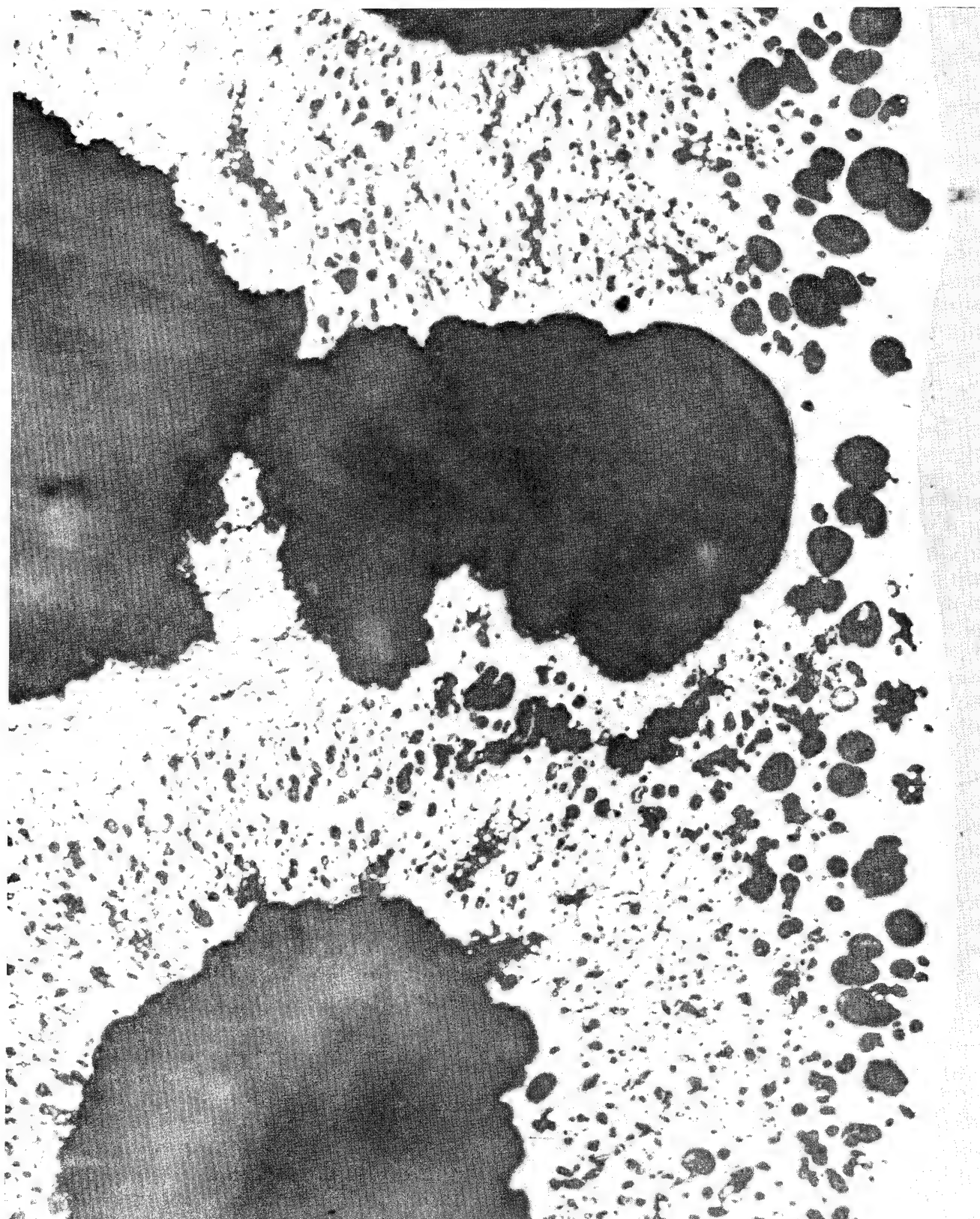
Figure A-9:   CROSS SECTION OF DRED GRAPHITE TWO IMPREGNATED WITH   3:1 RANDOM
               COPOLYMER (POLYMER 7, TABLE 2) X80

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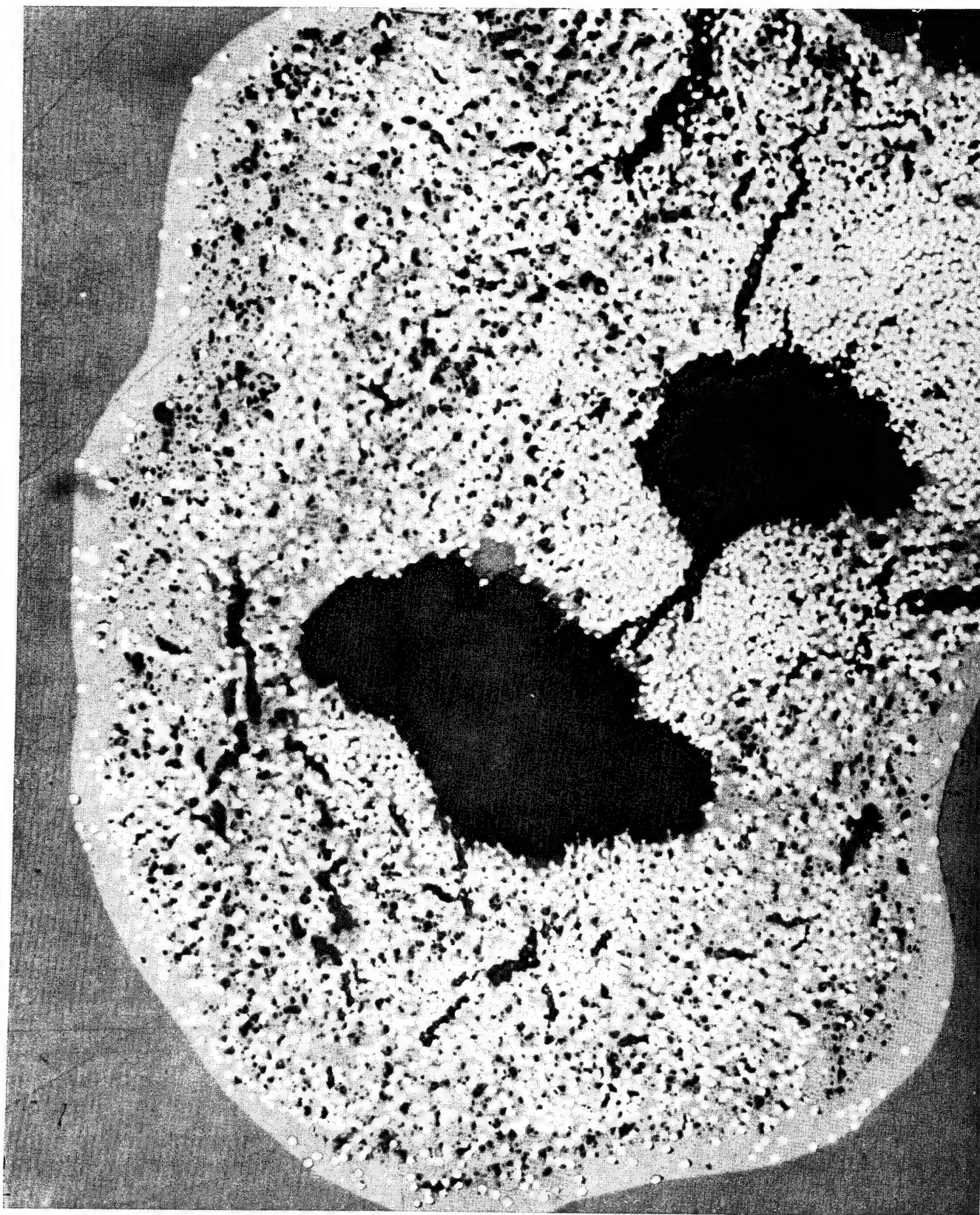
Figure A-10: CROSS SECTION OF DRIED GRAPHITE TOW IMPREGNATED WITH 1:3 RANDOM COPOLYMER (POLYMER 9, TABLE 2) X80

Figure A-11:   CROSS SECTION OF DRIED GRAPHITE TOW IMPREGNATED WITH 1:3 BLOCK
COPOLYMER (POLYMER 12, TABLE 2) X80
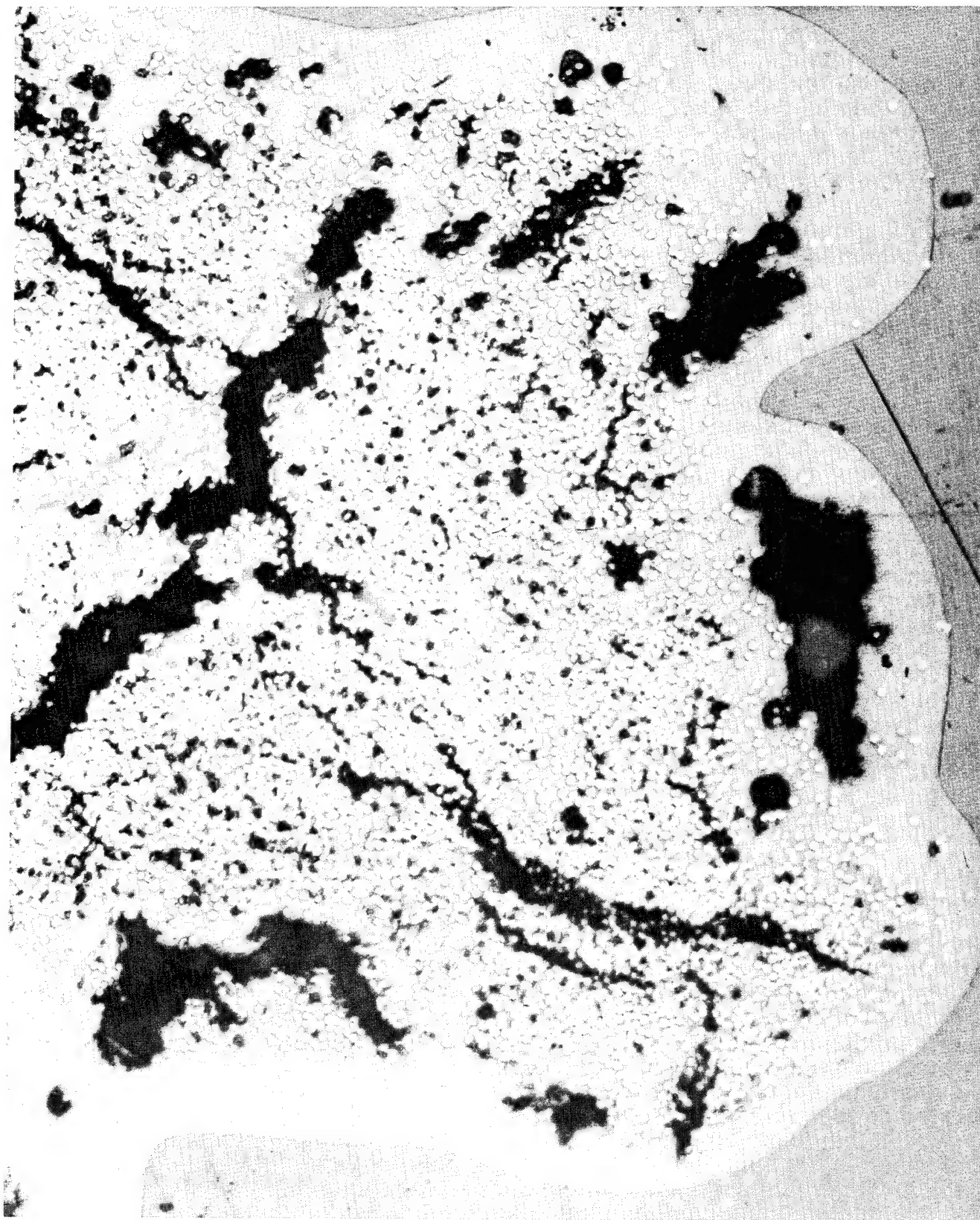
Figure A-12: CROSS SECTION OF DRIED GRAPHITE TOW IMPREGNATED WITH MEPPQ
(POLYMER 13, TABLE 2) X80

Figure A-13: ELECTRON PHOTOMICROGRAPHS OF ILS TEST FAILURE AREA,
LAMINATE 3, TABLE 8. X300
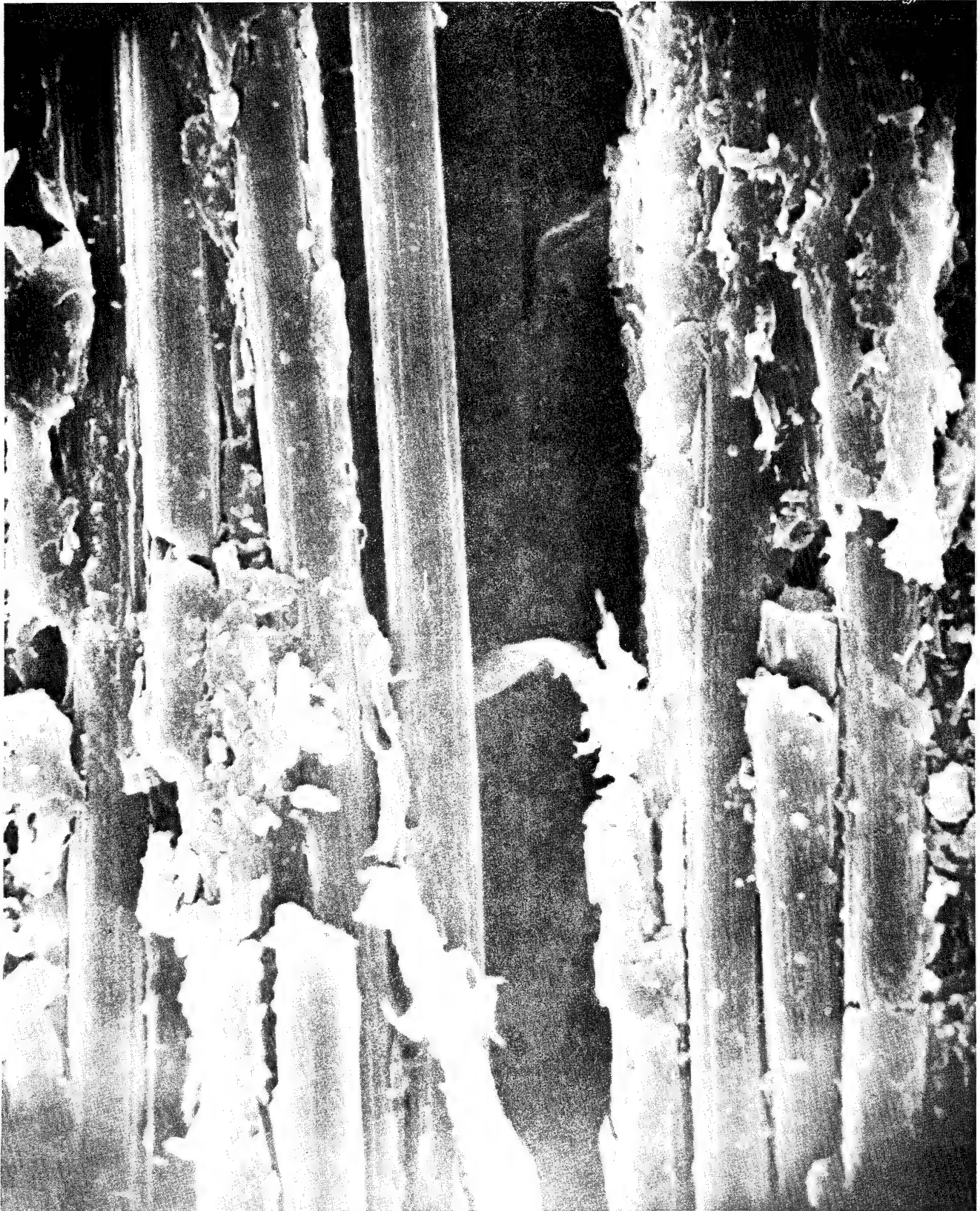
Figure A-14: ELECTRON PHOTOMICROGRAPHS OF ILS TEST FAILURE AREA,
LAMINATE 12, TABLE 8. X750

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Figure A-15: ELECTRON PHOTOMICROGRAPHS OF ILS TEST FAILURE AREA,
LAMINATE 17, TABLE 8. X300

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Figure A-16: ELECTRON PHOTOMICROGRAPHS OF ILS TEST FAILURE AREA, LAMINATE 23, TABLE 8. X300

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8.0 PROCEDURES AND TEST METHODS

8.1 Polymer Synthesis Procedures

Presented below are the detailed procedures used in the preparation of the reactants and the polymers utilized in this program.

8.1.1 Reactants

Para-Bis(Phenylglyoxalyl)benzene Para-Phenylenediacetic acid (566 g, 2.9 mole) melting at 249° -253°C(softened at 245°C) was stirred in thionyl chloride (1,7ℓ.) at RT for 48 hours to form a turbid orange solution. The orange solution was concentrated to near dryness at <50°C under vacuum to yield a yellowish orange solid which was washed with n-hexane and dried to yield the diacid chloride as yellow crystals (610g). The diacid chloride (619g, 2.6 mole) was dissolved in dry benzene (1.6ℓ) and added dropwise during 3 hours under nitrogen to a slurry of anhydrous powdered aluminum chloride (842g, 6.3 mole) in dry benzene (∿ 2.0ℓ) at < 10°C. After complete addition, the brown reaction mixture was stirred at < 10°C for 3 hours, and then overnight at ambient temperature. The resulting dark brown reaction mixture was poured onto ice in hydrochloric acid and stirred 4 hours to yield a gray emulsion. The thick emulsion was transferred to large evaporating dishes and allowed to sit overnight. After decanting the water and drying the residue at 75°C, the resulting solid was pulverized and washed successively with dilute aqueous hydrochloric acid, water, aqueous sodium carbonate, and water. The resulting dry gray solid (872g) was dissolved in DMF (5ℓ.), filtered, and cooled to yield light tan crystals which were washed with methanol and dried to afford p-diphenacylbenzene (573g), mp 204-207°C. To a slurry of selenium dioxide (404g, 3.6 mole) in glacial acetic acid (3ℓ), p-diphenacylbenzene (573g) was added and the mixture refluxed for 18 hours. The black mixture was filtered hot, and the yellow filtrate was treated with celite and charcoal, refiltered, and cooled to provide p-bis(phenylglyoxalyl)benzene (499g) as yellow crystals m.p. 124.5-126°C, [lit. m.p. 125-126°C (Ref. 7)] .

8.1.1   (Continued)

p,p'-Oxydibenzil

A mixture of diphenyl ether (340g, 2.0 mole) and phenylacetyl chloride (616.g, 4.0 mole) was added   dropwise during 5 hours to a slurry of anhydrous powdered aluminum chloride (553.2g, 4.2 mole) in methylene chloride (3l.) at 0°C under a drying tube. After complete addition, the brownish reaction mixture was stirred at ambient temperature overnight and then poured onto ice in hydrochloric acid. After sitting overnight, water was decanted and the residue was air dried. The resulting gray solid was successively washed with dilute aqueous hydrochloric acid, water, aqueous sodium carbonate, and water to provide a gray solid (790g, 97% crude yield), m.p. 163–167°C. Recrystallization was performed using DMF ($\sim$6l.) to afford p,p'-di(phenylacetylphenyl) ether (540g, 70% recovery), m.p. 169–171°C. To a slurry of selenium dioxide (270g, 2.4 mole) in glacial acetic acid (3l.) p,p'-di(phenylacetylphenyl) ether (475g, 1.2 mole) was added and the reaction mixture refluxed for 18 hours. The black mixture was filtered hot and the hot filtrate treated with charcoal and celite and refiltered. Upon cooling the filtrate, p,p'-oxydibenzil (383g, 75% crude yield on oxidation) separated as a yellow solid, m.p. 102–106°C. Recrystallization from ethanol provided yellow crystals (37% overall yield) m.p. 105–106.5°C [lit m.p. 106.4–107.4°C, (Ref. 18)].

3,3'-Diaminobenzidine

This material as received, melted at 174–176.5°C. Recrystallization was accomplished by dissolving 150g portions in deoxygenated water ($\sim$6l.) containing a pinch of sodium dithionite under nitrogen. The yellowish solution was treated with charcoal, filtered, and cooled to provide light tan needles (105g, 70% recovery) of the tetraamine, m.p. 176–177.5°C, [lit m.p. 179–180°C (Ref. 19)].

3,3',4,4'-Tetraaminobenzophenone

This tetraamine, m.p. 214–217.5°C, was recrystallized by dissolving 150g in DMF (1.5l.), and adding hot water ($\sim$3.0l.) to near turbidity. The yellowish solution was treated with charcoal, filtered, and cooled to afford the tetraamine (120g, 80% recovery) as yellow needles, m.p. 216–217.5°C, [lit m.p. 217°C, (Ref. 20)].

8.1.2   Polymers

Homopolymers (PPQ-I and PPQ-II)

The homopolymers were prepared according to the following representative procedure:

> p-bis(phenylglyoxalyl)benzene as a fine powder was added during 5 minutes to a slurry of the tetraamine in a mixture of m-cresol and xylene (1:1) (used ⌐ 70% of the original volume of solvent). The remaining solvent was used to wash down the residual tetracarbonyl reactant and the reaction temperature controlled by means of cooling in a water bath. The reaction mixture was stirred at ambient temperature for 18 hours to provide a viscous solution. A small portion of the solution was slowly poured into methanol in a Waring blender to precipitate a fibrous yellow solid which was then boiled twice in methanol. The yellow polymer was dried at 130°C in vacuo for 4 hours and characterized as shown in the various tables.

Films were prepared from all of the polymer solutions by doctoring a portion of the solution onto a glass plate followed by drying overnight at 70°C in air and then at 130°C in vacuo for 4 hours. All of the films were tough and flexible (fingernail creaseable) and various shades of transparent yellow. Thermaloxidative evaluation of polymer films is given in Tables 3, 4, 6, 7 and 15.

Random Copolymers

These copolymers were prepared following the same procedure as indicated for the homopolymers except that the tetracarbonyl reactant was added to a slurry comprised of a mixture of 3,3'-diaminobenzidine and 3,3', 4,4'-tetraaminobenzophenone according to the relative ratio given in Table 2.

Block Copolymers

The block copolymers were prepared in distribution ratio of biphenylene to benzophenone moieties of 3:1, 1:1, 1:3 as indicated in Table 2 through the following representative procedure.

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8.1.2   (Continued)

p-bis(phenylglyoxalyl)benzene (10.271g, 0.030 mole) as a fine powder was added during 5 minutes to a slurry of 3,3'-diaminobenzidine (5.357g, 0.025 mole) in a mixture of m-cresol and xylene (1:1, 40 ml). Additional solvent (12.5 ml) was used to wash down the residual tetracarbonyl reactant and the mixture stirred at ambient temperature for 18 hours to form a viscous clear orange solution.

In another flask, p-bis(phenylglyoxalyl)benzene (6.847g, 0.020 mole) as a fine powder, was added to a slurry of 3,3', 4,4'-tetraaminobenzophenone (6.057g, 0.025 mole) in a mixture of m-cresol and xylene (40 ml). Additional solvent (11.6 ml) was used to wash down the residual reactant and the mixture stirred at ambient temperature for 18 hours, to form a viscous clear orange solution.

The solution of the benzophenone oligomer was then added slowly with vigorous stirring to the solution of the biphenylene oligomer at ambient temperature. The viscosity rapidly increased, $\sim$ 10-20 min. (solids content, 20%) and additional solvent which was used to wash out the benzophenone oligomer's flask was added to reduce the solids content to 17.4%. Stirring was continued for 18 hours to provide a stable viscous orange solution of 1:1 block copolymer which is characterized in Table 2 (polymer No. 11).

8.2   Fiber Wetting Tests

Wetting tests were performed on polymer solutions adjusted to a nominal 17% solids. Solutions having solids content greater than 17% were standardized to 17% solids by dilution with a 1:1 meta-cresol-xylene solution. Polymer solutions of less than 17% solids were used in the as is condition (refer to Table 2). Table A-1 lists sets of specimens and experimental parameters used in the wetting tests. Essentially, a two-level experimental approach with two variables was used: rate of fiber bundle immersion (impregnation) into polymer solution, and solvent removal temperature.

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TABLE A-1 GRAPHITE FIBER BUNDLE WETTING EXPERIMENTAL CONDITIONS

Set Designation	Rate of Fiber Bundle ▷1 Immersion/Withdrawing From Polymer Solution	Drying Conditions ▷2	
		Temperature	Time
A	2.54 cm/min	121°C (250°F)	23 hr. ▷3
B	5.08 cm/min	121°C (250°F)	23 hr. ▷3
C	2.54 cm/min	232°C (450°F)	4 hr. ▷3
D	5.08 cm/min	232°C (450°F)	4 hr. ▷3

▷1   An electric driven apparatus precalibrated to give these rates was used to lower the bundle sections into individual polymer solutions.

▷2   The bundle sections were dried in an air circulating oven.

▷3   Initial drying was discontinued when a coupon consisting of a wetted fiber bundle section exhibited a weight loss (due to solvent evaporation) of less than .2% per hour. After the initial drying operation, all four sets were heated 1 hour at 399°C (750°F).

8.2   (Continued)

"Single" or groups of 10 or less fibers were impregnated by placing the fibers on glass slides wetted with a coating of the polymers solutions described in the above paragraph. The specimens were dried in an air circulating oven 1 hour at 177°C (350°F), 1 hour at 316°C (600°F), followed by 1 additional hour at 371°C (700°F).

8.2.1   Fiber Impregnation

Graphite yarn impregnation was accomplished by use of the apparatus depicted in schematic Figure A-17. Nominal yarn through put rate of 30 cm (12") per minute and drying tube temperature of 166°C (320°F) were used. These parameters yielded prepregs of nominally 50% solvent content by weight. After removal of the prepreg from the winding mandrel, the flattened prepreg was dried to the desired solvent content by allowing to stand in an air circulating oven at 149°C (300°F).

8.2.2   Prepreg Volatile Content

Prepreg volatile contents were initially determined gravimetrically by drying approximately 6.5 square cm (1 square inch) of prepreg at 316°C (600°F).

8.2.3   Resin Flow

The resin flow tests were performed as follows: AF-181-glass cloth, prebaked at 565°C, for 1 hour, was impregnated with each of the 13 polymer solutions listed in Table 5. Polymer solutions 5 and 12 had 13% and 15% solids, respectively, while the remaining systems were diluted to 17% solids content using 50% m-cresol xylene solution. Figure 7 shows resin flow test specimen configuration. The fabric was impregnated with four individual coats of polymer solution and dried after each coat at 121°C for the following periods of time:

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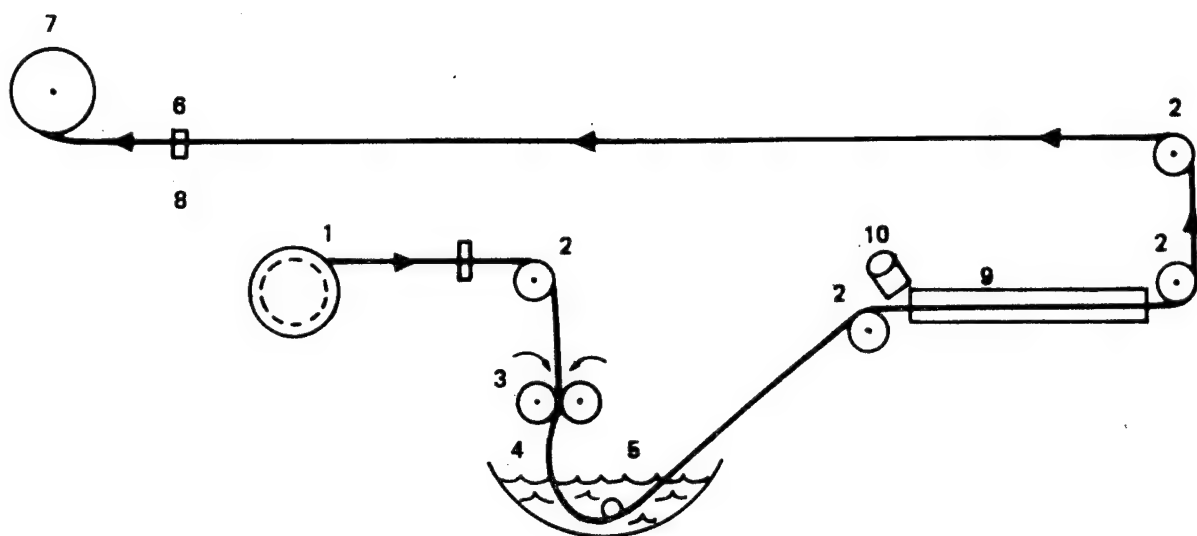
1. YARN ROLL
2. GUIDE
3. TEFLON ROLLERS DRIVEN AT SAME SPEED
4. FIBERS DECOLIMATE ON ENTRY INTO RESIN
5. STATIONARY GUIDE
6. WINDING GUIDE
7. WINDING MANDREL
8. BELT, YARN AND WINDING MANDREL DRIVEN AT SAME SPEED
9. DRYING TUBE
10. 1000 WATT HAIR DRYER

Figure A-17 : SCHEMATIC DRAWING OF IMPREGNATION — WINDING APPARATUS

8.2.3   (Continued)

First pass, 1 hour; second pass, 16 hours; third and fourth passes, 24 hours each.
After taking necessary weights to determine prepreg resin and solvent content,
the layup was placed between two 0.63 cm (1/4 inch) caul plates and inserted in
a heated press at 316°C (600°F) and pressed under 0.69×10^6 N/m^2 (100 psi) for
15 minutes. Measurable resin extrusion into the bleeder cloth or around the
periphery of the laminate, was not obtained using the above procedure. As
described in paragraph 3.1.1, interply adhesion was used as criterion for
resin flow.

8.2.4   Resin/Fiber Content

The method of resin content determination of PPQ laminates derived by digestion
in hot HNO_3 was found to be undesirable. This conclusion was based on the
observation that PPQ I composites yielded, after 14 hours digestion in hot (63°C)
concentrated HNO_3, fibers with visible resin residue. To avoid this source of
error, or error introduced by fiber oxidation through prolonged hot HNO_3
digestion, two alternate procedures for fiber/resin content determination were
briefly investigated. The first procedure consisted of determining the weight of
a one-foot length of impregnated, dried fiber bundle/resin system and comparing
this to the weight of a one-foot section of untreated graphite bundle. In the
second procedure, two prepreg specimens were taken from the center of a tape,
or near the middle of an impregnation run. One specimen was then dried at 316°C
(600°F) for 1-2 hours to determine the prepreg solvent content. The resin from the
second specimen was extracted with hot m-cresol (2-4 days at 63° ± 6°C) to
determine its fiber content. The resin content was then calculated from the relation-
ship of %R + %F + %S = 100. The test results obtained from each alternate pro-
cedure agreed very well and are described in Table A-2. The first procedure was
selected for use in this program.

8.2.5   Laminate Void Content

The void contents of laminates initially were calculated using measured density values
of laminates and comparing this to their theoretical density. The latter was
calculated by using the resin's density (measured), a fiber density value of 1.946/cc,
and a composite fiber volume of 50.00%. The percent void content,

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TABLE A-2   DETAILS OF ALTERNATE PROCEDURES FOR DETERMINING RESIN/FIBER CONTENTS

OF PPQ DERIVED LAMINATES

Procedure 1			Procedure 2	
Polymer PPQ 1			Polymer PPQ 1	
Weight 30 cm graphite fiber bundle [1]	F =	.282g	Prepreg Solvent (S) Content:	
Weight 30 cm fiber + resin [1]	F + R =	.477g	Weight F+R+S before drying [2]	1.212g
Weight resin in 30 cm treated fiber bundle [1]	R =	.195g	Weight F+R after drying [1]	.734g
Density Resin	r =	1.24g/cc	% S in prepreg	39%
Density fibers	t =	1.94g/cc	Prepreg Fiber Content	
Volume fibers in 30 cm (bundle)	V_f =	1.45cc	Weight F+R+S before extraction [3]	1.933g
Volume resin in 30 cm treated fiber bundle	V_r =	1.56cc	Weight F (after R+S extraction) [3]	.694g
% Volume resin - Actual		51.8 %	Weight F+R = 1.933 (.61)	1.179g
% Volume resin - Required		50% ± 2%	Weight R in prepreg	.485g
			% Volume Resin - Actual	52.2%
			% Volume resin - Required	50% (± 2%)

[1] m-Cresol was removed from impregnated tow by drying at 316°C (600°F) 24 hours.

[2] Prepreg specimen taken from center of an 28 x28 cm tape

[3] Prepreg R+S was extracted by adding m-cresol to prepreg and keeping the system at 63°C ± 6°C (145°F ± 10°F) for 4 days. At the end of each day, the m-cresol was replaced with fresh material. After final extraction the fibers were thoroughly washed with methanol then dried.

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calculated from the expression 100 (ρideal - ρmeasured) $\div$ ρideal, thus calculated yielded values ranging from 0.2% to 28.2% for the various laminates and cure parameters. Examination of high magnification cross section photoenlargements, Figures 9 through 12, reveal in many cases high void contents but none appear to be over 12-15%, indicating the theoretical void contents reported in Table 8 are too high. The good strength values, obtained under Task II described under paragraph 4.2 also support the above conclusion. In later portions of this program, the void content of laminates was determined by examination of laminate cross sections under high magnification.

8.2.6 Laminate Fabrication

Laminates were fabricated by press cure. Layups were prepared by overwrapping prepreg and bleeder cloths with steel shim stock described schematically in Figure A-18. Layups were then placed between caul plates preheated in a press set at the desired cure temperature and contact pressure. After allowing for residual solvent evaporation, the desired cure pressure was applied. Postcures were effected by raising the temperature of the press, at an overall heat up rate of 3°C per minute, without removing composites from the press.

8.2.7 Polymer Density

Polymer densities were determined by pycnometry using cast films of the polymers predried at 316°C (600°F) for 24 hours.

8.2.8 Elevated Temperature Aging of Laminates

Isothermal aging of laminates was effected in air circulating ovens preheated to the desired temperatures. Air velocities (Non-recirculting) were controlled to a nominal 150ml/min.

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SHIM STOCK
(2 MILS)

BLEEDER CLOTH
(AF 181)

BLEEDER CLOTH

EXPLODED VIEW

PREPREG LAYERS

COMPRESSED VIEW
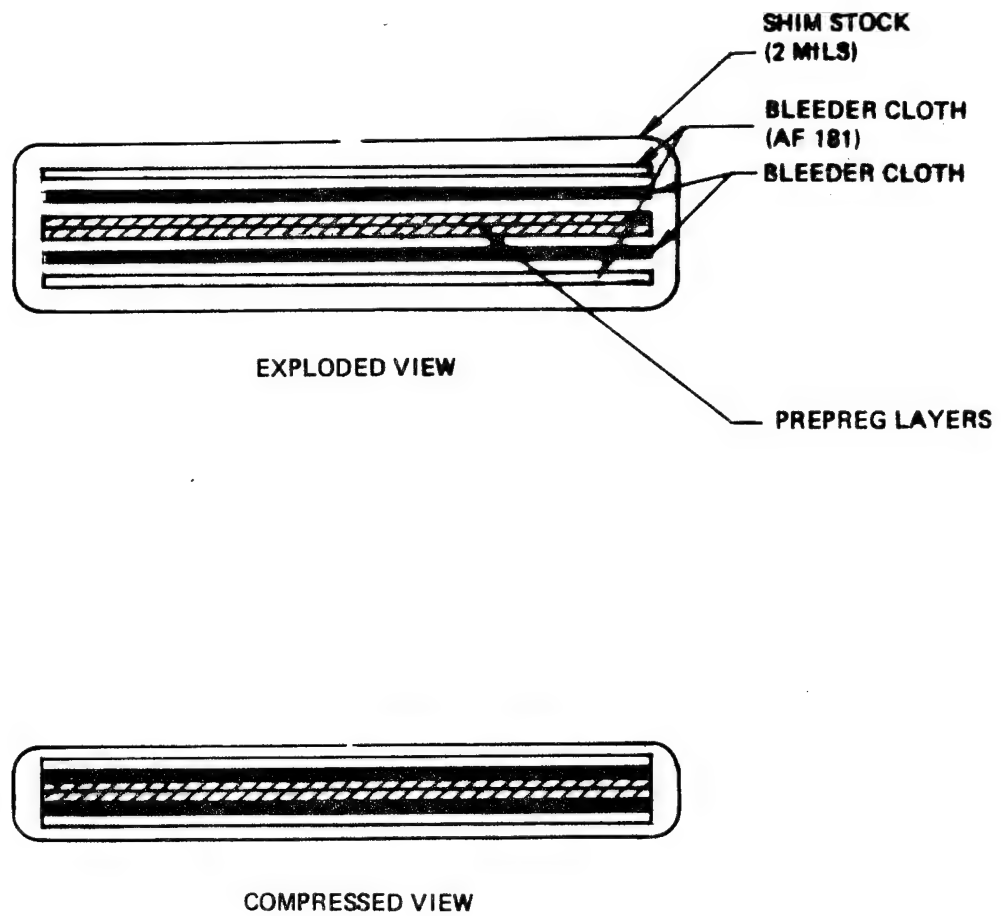
Figure A -18 : *SCHEMATIC DIAGRAM OF LAYUPS FOR CURING LAMINATES*

8.2.9　　　　Interlaminar Shear Strength (Short Beam)

All interlaminar shear (ILS) strength values reported were conducted using an FPS method (Reference 21). The tests were conducted per ASTM Test Method D2344. Test parameters and specimen configuration are shown in Figure A-19.

8.2.10　　　　Flexural Properties

Flexural properties were determined using an FTM specimen configuration (Reference 21). The tests were conducted essentially per ASTM Test Method D790. Test parameters and specimen configuration are shown in Figure A-20. All tests were conducted on an Instron test machine.

8.2.11　　　　Tensile Properties

Tensile strength and modulus were determined using an IITRI specimen configuration (Reference 21). The tests were conducted per ASTM test Method 638. Test parameters and specimen configuration are shown in Figure A-21.

8.2.12　　　　Creep Tests

Creep tests were conducted in accordance with Method 1063 of Federal Test Method Standard No. 406. Specimen were loaded and tested in tension at the test temperature. Creep measurements were made continuously throughout duration of the tests with extensiometers attached to the specimens.

8.2.13　　　　Thermal Expansion

Thermal expansion measurements were conducted in accordance with ASTM test method D696 using a Model TE-3000-L dilatometer manufactured by Thermo-Physics Corporation.

8.2.14　　　　Thermal Cycling

Composite laminates were thermally cycled between -53°C (-65°F) and 316°C(600°F) at a rate of 110°C per minute. For cool down, specimens were placed in a container

R = 1/8-IN. RADIUS
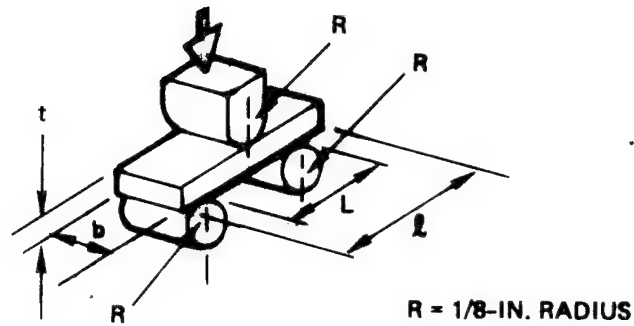
(1) DIMENSIONS AND CROSSHEAD SPEED

NOMINAL THICKNESS (t)	WIDTH (b)	SPECIMEN LENGTH (P)	SPAN L	CROSSHEAD SPEED
0.10″	0.25″	0.70″	0.50″	0.05″/MIN

(2) HORIZONTAL SHEAR STRESS CALCULATED BY CLASSIC FORMULAS

$$F = \frac{3P}{4A}$$

WHERE P AND A ARE THE LOAD AND CROSS-SECTIONAL AREA, RESPECTIVELY

Figure A-19: INTERLAMINAR SHEAR TEST SPECIMEN CONFIGURATION AND TEST PARAMETERS
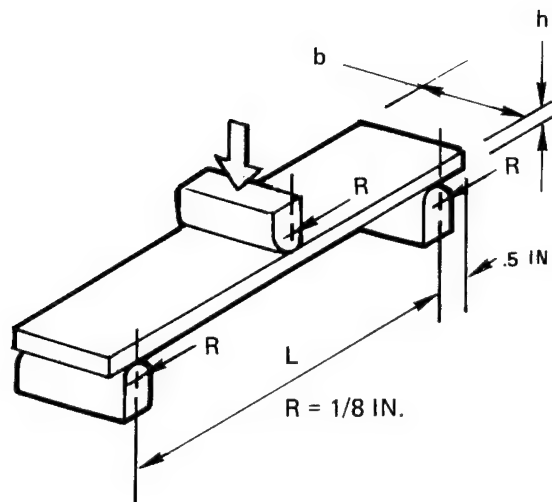
(1)   DIMENSIONS AND CROSSHEAD SPEEDS

NOMINAL THICKNESS	WIDTH b	SPECIMEN LENGTH	SPAN L
1/16"	0.5 "	2"	1"

(2)   FLEXURAL STRENGTH CALCULATED FROM THE FOLLOWING EQUATION:

$$F = \frac{3PL}{2bh^2}$$

(3)   FLEXURAL MODULUS

$$E = \frac{L^3 m}{4bh^3}$$

WHERE P, L, b, h and m ARE LOAD, BEAM SPAN, WIDTH, THICKNESS, AND SLOPE OF
   LOAD–DEFLECTION CURVE RESPECTIVELY

Figure A-20 : FLEXURAL TEST SPECIMEN CONFIGURATION AND TEST PARAMETERS

BONDED EPOXY
FIBERGLASS
END TABS
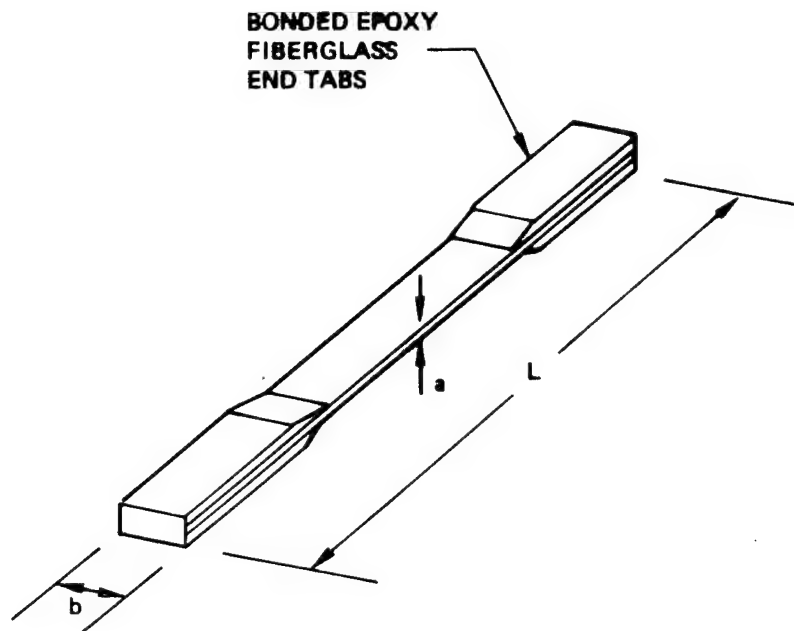
(1) NOMINAL DIMENSIONS

THICKNESS (a)	WIDTH (b)	TOTAL LENGTH (L)	TAB LENGTH (T)	CROSSHEAD SPEED
0.04″	0.50″	10″	2.25″	0.05″/MIN

Figure A-21: TENSILE TEST SPECIMEN CONFIGURATION AND TEST PARAMETERS

8.2.14   (Continued)

of .025 mm. (2 mils) thick FEP film and the system was immersed in a methanol bath held at -53°C. For heat up, specimens were removed from the FEP film container and placed in an oven held at 316°C. Specimens were allowed to soak for 10 minutes at each temperature extreme to reach equilibrium.

8.2.15   Hydrolytic Stability

Hydrolytic stability of laminates was determined by exposing the specimens to a 2 hour water boil environment. The test was conducted per ASTM Test Method D570. Test specimens were weighed before and after the water boil. The exposed specimens were tested for ILS strength at ambient temperature.

8.2.16   Elevated Temperature Tests

All elevated temperature flexural, ILS, and tensile tests were conducted at the temperatures specified after a specified heat soak at temperature. The heat soak times were determined experimentally. Three specimens of different known thicknesses were prepared with a thermocouple imbedded at the center of each specimen. The specimens were exposed to the test environment with a second thermocouple located at the specimen's surface near the imbedded thermocouple. The time lapsed for the imbedded thermocouple to reach the test temperature, as registered by the surface thermocouple, was considered the heat soak time for that particular thickness. Three such measurements were made at 204°C and three at 316°C. The results are summarized in Figure A-22.
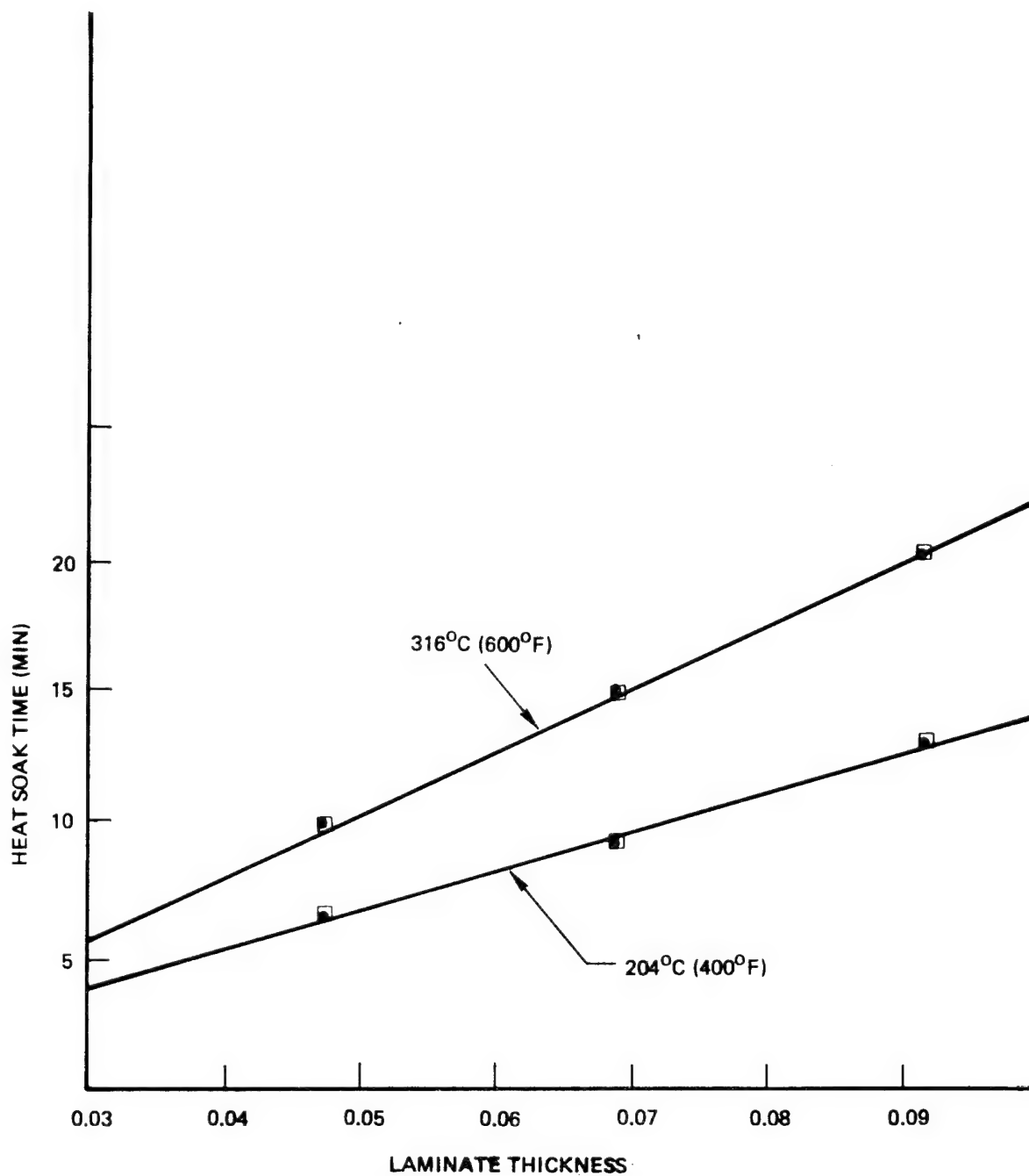
Figure A-22 HEAT SOAK TIME VERSUS LAMINATE THICKNESS

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